A MANUAL OF RADIOACTIVITY

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PREFACE

TO THE

ENGLISH EDITION

In writing our manual on " Radioactivity " our main aim was to satisfy the requirements of the student, and it is a source of real pleasure to us that our book is now appearing in English.* The present edition is not a literal translation of the original ; it is essentially a new edition, and we have availed ourselves of the opportunity of incorporating the results of scientific advances made since the appearance of the first German edition. Whereas the latter took account of the literature in general only up to the beginning of the year 1922, the present edition, both in the text and in the bibliography (Appendix), embodies the results of research work published up to the early part of 1925. Particularly the sections relating to atomic structure have been considerably modified and extended. Moreover, our attention has been directed to several errors in the German text, and these have now been rectified.

Our best thanks are due to the publishers, at whose suggestion the translation was undertaken, and to the printers for the great care they have taken in the production of the book and in the preparation of the illustrations. We desire also to thank those research workers who have contributed to the success of the illustrations by kindly supplying photographic prints of certain figures, and also the societies and publishers who have granted permission to reproduce these and other illustrations

(see p. xix).   Finally, we offer our heartiest thanks to our former colleague, Dr. Lawson, not only for his painstaking translation but also for his expert assistance in the improvement of various sections of the book.   We join with him in expressing our indebtedness to Dr. Arthur Holmes (University of Durham) for his kindness in looking over the proofs.

G. HEVESY.
F. PANETH.

January, 1926

PREFACE

FIRST GERMAN EDITION

THE purpose of the present volume is sufficiently indicated by its title ; it is intended to be a *Manual* of Radioactivity.

There already exist several exhaustive works on radiology for the advanced student and the research worker, and detailed monographs on certain branches of the subject have been published from time to time. Nevertheless, it has been our experience, and doubtless many of our colleagues have been faced with the same difficulty, that students—in physics, chemistry, and medicine—invariably ask the question as to which is the most suitable book from which to get an insight into the science of radioactivity at first hand, and without the presupposition of an elementary knowledge of the subject. Owing to the wide range of the subject, this is by no means an easy question to answer.

In view of this fact, we have attempted to select and arrange the subject matter so as to give prominence to the didactic points of view, somewhat in the same manner as has long been done in every text-book on the related sciences of physics and chemistry. Whereas in the early days of radioactive research, before the relation between the numerous remarkable observations was recognised, it was convenient to make use of the historical development of the subject as an introduction to the new science, we believe that the time is now opportune for completely separating the didactic from the historical development of radioactivity. Our meaning will be clear if we remind the reader that a text-book or manual of chemistry does not begin with a description of the misconceptions of the alchemists, but rather with the much more instructive experiments of a quantitative nature on the composition of water, etc., in spite of the fact that they belong to a much later period and are more difficult to carry out. At the same time, we do not consider the historical development to be uninteresting, and students who are

already familiar with the elements of the subject will find in the concluding chapter a résumé of progress in radioactive research from its inception until recently, together with an indication of the part played in that work by the various research laboratories.

In the choice of our material we have also been guided by pedagogical motives. Although we have endeavoured to present the fundamentals in sufficient detail to render them readily intelligible to the reader, some of the later chapters have perforce had to be treated in a brief manner. At this point the study of special treatises and scientific journals should begin, but we hope that from amongst the most important of the more recent problems, which have not yet found a place in the available works on radioactivity, we have at least made accessible the main content. We have only introduced the principles of the methods of measurement used in radioactivity, and not the practical manipulative instructions, here again we find justification in the accredited procedure of text-books on physics and chemistry, which leave technical laboratory details to the treatises on practical physics, or analytical and preparative chemistry. We were more readily able to adopt this course in view of the fact that, for the purpose of radioactive measurements, we already possess the excellent book on this subject referred to below.

For the purpose of a more exhaustive study of the science of radioactivity, we would draw attention, in particular, to the following books :

E. Rutherford, " Radioactive Substances and their Radiations," Cambridge University Press, 1913.

Mme. P Curie, " Radioactivité," 2 volumes, Paris. 1910.

St. Meyer and E. v. Schweidler, " Radioaktivität," Teubner. Leipzig, 1916 (Revised Edition in the Press)

Smaller works, dealing with special branches of the subject, include the following :

F. W. Aston, " Isotopes," 2nd Edn , Arnold, London, 1924.

J. Chadwick, " Radioactivity and Radioactive Substances," Pitman, London, 1921.

Mme. P. Curie, " L'isotopie et les éléments isotopes," Blanchard, Paris, 1924.

K. Fajans, " Radioactivity," translation by Wheeler and King. Methuen, London, 1923.

F. Henrich, "Chemie und chemische Technologie radioaktiver Stoffe," Springer, Berlin, 1918.

A. F. Kovarik and L. W. McKeehan, "Radioactivity"; Nat. Research Council, Bull. 10; pp. 203; March, 1925.

A. S. Russell, "An Introduction to the Chemistry of Radioactive Substances," Murray, London, 1922.

F. Soddy, "The Chemistry of the Radio-Elements," Part I., 1911; Part II., 1914; Longmans, Green & Co., London.

For the methods of measurement used in radioactivity the following book is of primary importance :

W. Makower and H. Geiger, "Practical Measurements in Radioactivity," Longmans, Green & Co., London, 1912.

Furthermore, mention should be made of Chapter 169 in the *Lehrbuch der praktischen Physik*, by F. Kohlrausch (Teubner, 14th Edition, Leipzig, 1923), and Chapter V. in Meyer and Schweidler's *Radioaktivität*. The most important methods for chemists are also contained in the new edition of the *Hand- und Hilfsbuch für physikochemische Messungen*, by Ostwald-Luther-Drucker, which is in preparation.

As regards radiology in medicine, the following books deserve mention :

F. Gudzent, "Grundriss zum Studium der Radiumtherapie," Urban and Schwarzenberg, Berlin, 1919 ; it gives a very complete review of the extensive literature on the subject up to the year of publication.

H. A. Colwell and S. Russ, "Radium, X-Rays, and the Living Cell," Bell, London, 1924.

With regard to original papers, they can be readily traced by reference to the larger treatises, particularly the book of Meyer and Schweidler. But since the last-mentioned volume only takes account of the literature on the subject up to the year 1916, we have considered it advisable, in the case of papers on which our account of the later and most recent results of research is based, to give the references to such publications in notes at the end of the book. The numerical references in the text direct attention to these notes, which are arranged consecutively, chapter by chapter, and embrace more or less completely the publications in radioactivity that have appeared since 1916.

We are indebted to various colleagues—in particular to Messrs. Dirk Coster, Hans Geiger, Hans Kramers, Robert W. Lawson, Svein Rosseland, and Frl. Lise Meitner—for their kindness in reading over those chapters which deal with the branches of research on which they are engaged.

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July, 1922.

Note.—The above differs from the original inasmuch as references to more recent literature have been added   R W L

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ACKNOWLEDGMENTS

I

INTRODUCTION

1. FUNDAMENTAL EXPERIMENTS

THE science of radioactivity derives its name from the chemical element radium, which was discovered in the year 1897, and it was mainly with this substance that the unique phenomena have been observed, the study of which forms the basis of this new science. Radium is obtained by separating in the form of the chloride the slight traces of barium contained in uranium minerals, and then subjecting this chloride to fractional crystallisation Under such treatment, the more difficultly soluble fractions become richer in the chloride of radium, which in this manner can finally be obtained in a chemically pure state.* From the chemical viewpoint the salts of radium (chloride, bromide, carbonate, sulphate, etc.) and metallic radium bear a great resemblance to the corresponding compounds of barium and to metallic barium respectively, but they differ from this and from practically all other chemical elements by virtue of certain special properties. We shall discuss the most important of the experiments which show this peculiarity of radium, but at this stage we shall refrain from the discussion of the experimental difficulties which some of them offer. In these experiments we may use a few centigrams of radium chloride, contained in a small glass tube with sealed ends.

(1) If the glass tube be laid for a few seconds on a photographic plate, then after development the plate is found to be strongly blackened where the tube was situated ; at greater distances the plate is less strongly affected.

(2) A screen coated with barium platino-cyanide, such as is used in detecting the presence of Röntgen rays, is also found to become luminous when the tube containing radium is brought near it.

(3) A charged electroscope loses its charge when the tube is situated near it.

(4) Very small quantities of two different gases, helium and

Further details of the mode of preparation are contained in Ch. XXIII.

S.P.R.   A

emanation, gradually accumulate within the tube, and can be detected by the methods of micro-gas analysis.

(5) If the glass tube be exceedingly thin, but at the same time quite airtight, the appearance of the gas helium can also be observed outside of the tube.

(6) The tube has always a slightly higher temperature than its surroundings.

In the explanation of these remarkable properties we are especially aided by experiment (4) By means of the most accurate chemical analysis we are able to detect initially only the two elements radium and chlorine in the form of the solid compound $RaCl_2$. After the lapse of a few days or weeks, however, the tube contains an exceedingly small quantity of a gas mixture, the spectroscopic examination of which, in addition to helium, reveals the presence of an element previously unknown, and called emanation. Owing to the nature of its spectrum, and because of its inability to take part in chemical reactions, this element, like helium, must be included amongst the rare gases. Thus, two new elements have been derived from radium chloride, and since the same results can be obtained by using radium bromide, radium carbonate, etc., and metallic radium, we are led to the conclusion that it is the element radium that has been transformed into the other two chemical elements.

Quantitative experiments supply us with a clue as to the manner and nature of this transformation. If we seal off 1·3138 gm. $RaCl_2$ (containing 1 000 gm. of the element radium) in an evacuated tube, we should be able to establish by the methods of micro-gas analysis, that after four days 0 311 mm.^{3} of emanation have been produced (measured at 760 mm. pressure and at 0° C.), whereas the amount after eight days would be 0 463 mm.^{3}, and after thirty days 0·607 mm.^{3} Moreover, we should find that no matter how long we wait, even after several years, this last value would not be exceeded. With helium, on the other hand, we should find that if we neglect the growth during the first few days, the accumulation of helium would be proportional to the time that had elapsed since the tube was sealed off, so that after one year we should find approximately 167 mm.^{3} of helium, and after two years twice this amount, and so on.*

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* The above relation does not hold quite accurately owing to the fact that in the course of several months an appreciable quantity of polonium has been formed, and the generation of helium from this source must also be taken into account.

This difference in the behaviour of helium and emanation must find an explanation in the nature of the two gases. In order to investigate this point, we shall suppose them collected separately, and observe their behaviour during the course of an extended period of time. The helium is found to remain unaltered, and no matter how long we keep it, the volume remains constant. The behaviour of the emanation, however, is quite different. Initially it was completely free from helium, but after the course of a few days we are again able to detect the presence of this gas in the emanation, whereas the amount of emanation constantly diminishes. After the lapse of four days only one half of it is left, after eight days only about one quarter, and after a month only about one thousandth of the original quantity of emanation remains. This process is accompanied by another surprising phenomenon, which is of particular importance in the interpretation of the process; a deposit of lead is found to form on the walls of the vessel in which the emanation has been contained. The quantity of lead formed is simply related to the amount of emanation that has disappeared; in place of each atom of the latter, an atom of lead makes its appearance, and hence the quantity of lead increases during the first four days to one half of its maximum amount. After one month the amount of lead remains practically constant.* Furthermore, it can be shown that the emanation tube gives rise to all the phenomena described under experiments (1), (2), (3), (5) and (6), which we were able to observe with the tube containing radium.

2. The Hypothesis of Atomic Disintegration

Without exception it has been found possible to explain all the above-mentioned observations and experiments by means of a theory, which also embraces many other related phenomena not touched on here, and which rendered possible the correct prediction of phenomena as yet not discovered. This theory is based on a single hypothesis, in principle quite novel, namely, the assumption of the disintegration of the atoms of chemistry.

Before the discovery of the radioactive elements it had been possible to attribute the whole of the phenomena in physics and chemistry to the behaviour of the atoms and of their association in the form of molecules. In spite of numerous experiments, science had never succeeded in establishing the transformation of one

* Later on we shall deal with the properties of the lead so produced. It is called Radium D.

chemical element into another, and since we regard the atoms as the carriers of the properties of elements, we were forced to the conclusion that chemical atoms remain unaltered under all circumstances. This conception does not stand in contradiction to the fact that, in many processes such as the emission of light, ionisation, and the formation of chemical compounds, certain properties of the atoms disappear, and others take their place. We need only assume that the essential nature of the atom is maintained, and that only relatively minor changes take place, which can always be made retrogressive.*

Since the new elements helium and emanation are formed from radium, we must assume in this case that atoms of helium and of emanation are produced from the atoms of radium. Here we are confronted with a disintegration of the radium atom, and this process is not reversible. In spite of experiments on these lines, it has never been possible to detect the formation of radium from helium and emanation. This property of disintegration is associated not only with radium, but also with emanation, as mentioned above, which is transformed in its turn into other elements. The same feature characterises a large number of other radioactive substances, with which we shall become acquainted later on. Previously established conceptions in chemistry and physics were of no avail in the face of these facts, and it became necessary to develop a new science, the Science of Radioactivity

Like the word *radium*, the term *radioactive* was chosen in this new science, because the first phenomenon to receive attention was the emission of particularly characteristic rays (*radius* = ray) by such substances ; not until later was it noticed that these rays solely represent phenomena accompanying atomic disintegration, and for this reason we now define a substance as being radioactive when the atoms of which it is composed disintegrate spontaneously, and regardless of whether or not the emission of rays can be detected in the process.

The phenomena that were mentioned in connection with our basal experiments (1) to (6) all represent effects produced by these rays ; we shall be made familiar with the nature of the rays in a later chapter specially devoted to this aspect of the subject. At this stage it will suffice to mention that they are not only useful for the

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* We shall have occasion in what follows to discuss what we have to understand by the " essential nature of the atom," in the light of more recent theory.

qualitative detection of radioactive substances, but they can also be utilised with especial advantage in the quantitative measurement of such substances. The intensity of each type of ray is simply proportional to the available quantity of the substance emitting it. Instead of the above-mentioned chemical or gas-analytical method of detection of the quantity of a radio-element, which is in practice a very irksome business, we almost always make use of the measurement of its radiation in the determination of the amount present. For this reason it is imperative that we should have an accurate knowledge of the rays, and of the methods used in their measurement.

3. The Rays emitted by Radioactive Substances

In order to render this section more readily intelligible, it will be of advantage to call to mind the different theories that have been formulated as to the nature of rays of light, and other types of rays well known to physicists. Whereas Newton assumed that rays of light consisted of a swarm of very quickly moving material particles, Huyghens' conception was that we are not dealing with the propagation of material constituents, but with that of a state of motion. According to his theory, which, after much tedious discussion and numerous experiments, was found to be more prolific in the case of light than Newton's theory, we have to regard a ray of light as consisting of the propagation of a state of vibration in the aether. Later, the same two alternatives presented themselves in the case of the cathode rays and Röntgen rays. Here again both modes of explanation found distinguished protagonists, until finally for cathode rays the emission theory, and for Röntgen rays the wave theory held the field.

In the case of radioactive substances it is not possible to come to a simple decision one way or the other, for here we are confronted by both types of rays, some of them being material in kind and others resembling light. The so-called α- and β-rays are corpuscular, whereas the γ-rays, like the closely related Röntgen rays, are nothing else than a form of light of very short wavelength. The common property of all these rays, and the reason for grouping them together under this name, is to be found in the fact that they transmit energy rectilinearly and with great velocity through space.

As already mentioned, before the discovery of the rays emitted by radium, other rays had been observed that were necessarily

regarded as corpuscular in nature, in contrast to those of light. Thus the cathode rays, which result from the application of a high voltage across a highly evacuated tube, consist of a swarm of particles of negative electricity, of so-called electrons ; and in the same tube we can detect particles flying in the opposite direction, *i.e.* towards the cathode, and these are called positive rays According to the gas previously contained in the tube (oxygen, carbon dioxide, mercury, etc.), they consist of molecules and atoms of different chemical elements and compounds, associated with positive electrical charges. β-rays are identical in nature with the former cathode rays, whereas the α-rays show a marked similarity to the latter positive rays.

Our knowledge of the nature of the rays emitted by radium was obtained from experiments on their deflection and absorption The following diagram (Fig. 1) shows schematically the action of a strong magnet on a pencil of α-, β-, and γ-rays emitted from a narrow opening and in a rectilinear direction. In this diagram the magnetic field is supposed to be directed perpendicularly to the plane of the paper, with the north pole of the magnet above that plane. The α-rays are slightly deflected to the left, whereas the β-rays suffer a much greater deflection to the right. If the magnetic field is sufficiently strong, the β-rays are bent into complete circles, but the γ-rays are wholly uninfluenced by the magnetic field. From the direction of the deflection we are able to determine whether the charge on the particles is positive or negative, and from the magnitude of the deflection, combined with similar deflection experiments in an electric field, the magnitude of the specific charge (e/m) and the velocity of the α- and β-particles can be determined.

FIG 1   Action of a Magnetic Field on α-, β-, and γ-Rays

Another fundamental experiment consists in testing the absorption of the rays, *i.e.* the diminution of their intensity after they have passed through matter, whether this be in the gaseous, liquid or solid state. Whereas the γ-rays are only slightly weakened in intensity by the introduction of an aluminium plate 5 mm. thick in the path of the rays, the α-rays are completely, and the β-rays almost

completely absorbed by the plate. On the other hand, a thin sheet of paper or of aluminium of thickness 0·1 mm. is insufficient to hold back the β-rays, whereas it is wholly effective in preventing the passage of α-rays. In this way then, we have, together with magnetic and electric deflection experiments, a simple means of separating the different types of rays from each other. We shall deal in the next section with the methods of measuring the intensities of the rays.

4. METHODS OF MEASUREMENT FOR THE RAYS FROM RADIUM

Every well-defined action of the rays from radium can of course be utilised, in principle, for the purposes of their quantitative comparison. Thus it is very simply shown that radium preparations do not change appreciably in the course of a year, by comparing with each other the blackenings they produce in a given time on a photographic plate (cf. Fundamental Experiment 1), but very exact results cannot be obtained in this manner   Moreover, in quantitative work we should hardly have recourse to the heating effects of radium (Fundamental Experiment 6), since they can be accurately measured only with very strong preparations.* The best and most general method has been found to be the action of the rays on gases, which conduct electric charges in consequence, and thereby lose their insulating properties (Fundamental Experiment 3).

Let us suppose we have a positively charged hemispherical shell of copper, the edge of which rests on a slab of a good insulator, e.g. paraffin, and for the rest is surrounded by air. The charge on the hemisphere flows to earth as soon as we touch it with a wire, the other end of which is connected to earth ("earthed"). Left to itself, air is not capable of conducting electricity, but if we bring a radium preparation near to the hemisphere, the air becomes conducting, and the electricity now flows through the air in much the same way as if we had brought an earthed conductor in contact with the sphere. The air is "rendered conducting" by the rays from radium, and the degree of conductivity is greater, the stronger the radium preparation with which we are working.

A slight adaptation of the apparatus just described will serve as an exact measuring instrument. In order to measure the conductivity imparted by the rays from radium to a definite and well-defined

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* We shall make the acquaintance later of an exceptional case, in which the heating effect is used with advantage for the measurement of radioactive substances (see Ch. XXIV, Note 32).

quantity of air, we use the inside of the charged hemisphere. As nearly as possible in the middle of the sphere is situated a circular metal plate resting on the paraffin slab. Connected to this metal plate is a wire, which passes through the slab and is attached to one terminal of a galvanometer, the other terminal of which is earthed, as seen in Fig. 2. The preparation to be measured is laid on the metal plate, the hemisphere is placed over it, and this is connected to a source of potential of from 1000 to 2000 volts. If the preparation
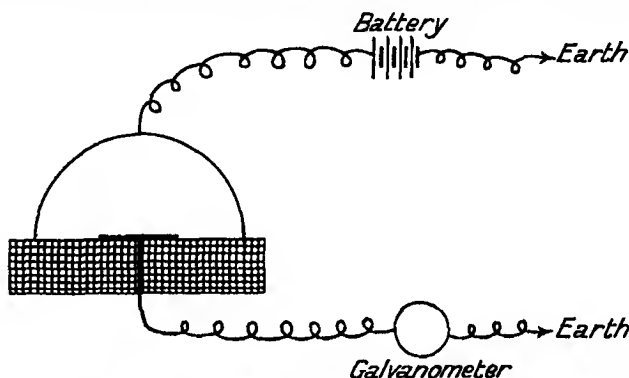
FIG 2   Apparatus for Measuring Strong Radioactive Preparations

is not radioactive, the air within the hemisphere will remain an insulator, and electricity cannot flow from it to the metal plate and thence to the galvanometer. But if in consequence of the rays emitted by the radium preparation the air between the hemisphere and the plate is " ionised," a quantity of electricity corresponding to the strength of the ionisation passes from the hemisphere to the plate and through the galvanometer to earth. Thus the current registered by the galvanometer is a direct measure of the ionisation produced in the enclosed air, and hence also of the strength of the radium preparation, provided that the applied potential is sufficiently high to ensure that the maximum current, the so-called " saturation current," in the ionised air is attained. If the applied potential is insufficient for saturation, a more complicated relation results, which, we shall now briefly discuss.

When we gradually increase the potential of the outer hemisphere for a preparation of given strength, it is found that the current grows rapidly at first, and then more and more slowly, as indicated in curve A of Fig. 3. When the potential exceeds a certain value, the current remains constant. For a stronger preparation the shape of

the curve is similar, but it attains a higher constant value (curve B).
Thus, whereas for small applied potentials the strength of the current
depends both on the potential and on the strength of the preparation,
after a certain high value of the potential has been reached the
current is then only a function of the strength of the preparation, and
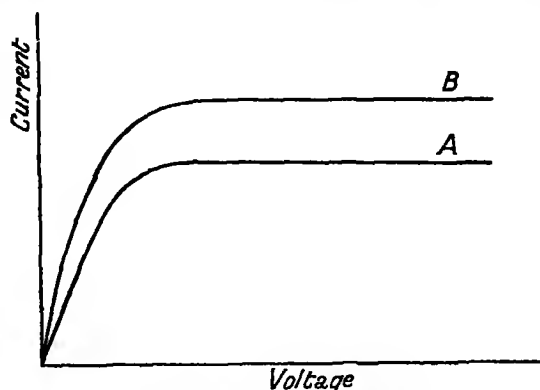
FIG 3　Attainment of the Saturation Current

can therefore be used as a measure of that strength (Saturation
current). By maintaining quite constant experimental conditions
it is of course possible to compare the strengths of preparations with
incomplete saturation, and for experimental reasons we are obliged
in many measurements to forgo the advantage of attaining complete
saturation. This is particularly the case with α-rays, which produce
many more ions per cm. of their track than β-rays (see p. 38), and
it is often impossible to attain saturation with them.

The galvanometric measurements described above can only be
carried out with very strong preparations, because the saturation
currents obtainable in air are always very weak (see p 15, Note),
and hence we are compelled to use other more sensitive apparatus,
such as is not otherwise used in the measurement of current. For
this purpose the electroscope occupies a foremost position. In its
simplest form, this well-known instrument consists of two strips of
gold or aluminium foil attached at their upper ends; on charging
them, the strips diverge. The amount of this divergence is greater
the more strongly they are charged, and in electroscopes that have
been adapted as measuring instruments, the divergence of the leaves
can be read off on a scale placed behind them. Under normal
conditions, the leaves remain deflected for a long time, and only
gradually collapse (" natural leak "), for the air has very pronounced

insulating properties. But if we bring a radium preparation into the neighbourhood of the electroscope, the leaves collapse more or less quickly in accordance with the degree of conductivity that the preparation is able to impart to the air. If one preparation is twice as strong as another, it imparts to the air twice the conductivity, and hence the leaves collapse at twice the rate, provided that the experimental conditions are maintained the same in the two cases. Thus the time required by the leaves to pass over a given number of divisions of the scale is inversely proportional to the strength of the preparation. Here also the magnitude of the saturation current serves as a measure of the ionisation. If the scale of the electroscope is graduated in volts, and the capacity (C) of the entire measuring system, measured in cms , is known, we can calculate the saturation current in the following way : Suppose the leaves collapse from V_1 to V_2 in t seconds, then the drop in voltage is ($V_1 - V_2$), and the quantity of electricity that has leaked away is hence $C(V_1 - V_2)$. Since 1 volt $= \frac{1}{300}$ electrostatic units, we must divide the above result by 300 in order to obtain the saturation current in electrostatic units. Thus our final expression is

$$i_{(sat)} = C \cdot \frac{V_1 - V_2}{300t} .$$
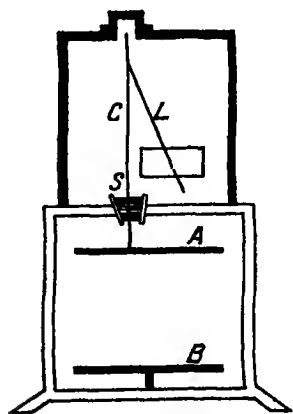
The exceeding simplicity of its use, its rapid action and its small cost make the electroscope the most favoured instrument in radioactive work.

According to the purpose for which the electroscope is primarily required, we differentiate between different types of instrument. Fig. 4 shows a so-called "α-ray electroscope," i.e an electroscope which, although it permits of the measurement of all three types of rays, has in general too small a sensitiveness for the relatively smaller action of the β- and γ-rays In this electroscope we have an ionisation chamber

FIG 4 α-Ray Electroscope

AB into which the preparation is introduced, and it is separated by an amber or sulphur insulating plug S from the chamber in which the electroscope leaf (L) is situated. Passing through the plug S and connected with the plate A is a thin metal rod C, which is charged to a definite potential when the instrument is in use, whereas the plate B is directly connected to the earthed outer metal vessel.

In " β-ray electroscopes " (see Fig. 5) the ionisation chamber and the measuring chamber are combined, in order to diminish the capacity and hence to increase the sensitiveness. In the base of the instrument there is an opening which is only closed by a thin aluminium foil W; this prevents the a-rays from passing into the instrument, but does not deter the β-rays. The walls of the vessel are of sufficient thickness to prevent the entrance of β-rays. The active preparation is centrally placed beneath the aluminium foil. As γ-rays are also often present, they are measured with the β-rays in such a β-ray electroscope, but their effect can generally be disregarded as compared with that of the β-rays. The same electroscope can also be used as a ' γ-ray electroscope," if we close the opening W by means of a metal plate of the same thickness as the walls of

FIG 5
β-Ray Electroscope

the electroscope, instead of by aluminium foil. The electroscope is charged through the bent wire B. which rotates in the insulating stopper C, and can thus be brought into contact or otherwise with the insulated system below the insulating plug S.
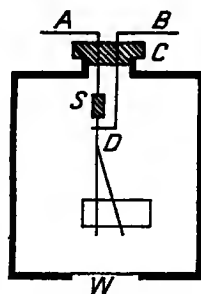
If we require to make measurements with a gaseous radioactive substance, we make use of a so-called " emanation electroscope."

FIG 6   Emanation
Electroscope

In this instrument the ionisation chamber is a closed airtight vessel Fig. 6 illustrates one of the many possible forms of this instrument.

In general we require to establish the presence " of radioactive substances, and in such a case comparative measurements adequately fulfil our purpose. But if we desire to carry out absolute measurements. we must be able to determine the absolute value of the saturation current, and from what has already been said it will be clear that in this case we must know the capacity of the instrument and the voltage calibration of the scale of the electroscope. We shall refrain from discussing the methods of measurement in greater detail here, as they are to be found in the special works referred to in the Preface.* It should be mentioned, however, that in many

* For convenience, several different units have been introduced for the measurement of radioactive substances (1 Curie, 1 Mache, 1 Eve, etc.). These different units are dealt with in Chapter XXIV, under the headings of radium and radium emanation.

of the more recent instruments the metal leaves of the electroscope have been replaced by fibres of platinised quartz, and this arrangement has been found to be of great service.   In the " single fibre " instrument the insulated fibre is fixed at both ends and situated between two metal plates connected to the poles of a battery of about 40 volts, the mid-point of which is earthed.   When the fibre is charged, it is attracted towards one or other of these plates, and during a measurement the motion of the fibre is observed by means of a microscope with an eye-piece scale.   In the " double fibre " instrument, the two adjacent insulated fibres are attached at both ends, and repel each other when charged, so that the subsidiary voltage plates are unnecessary.   As before, readings are taken with a microscope with an eye-piece scale.   In many cases it is preferable to measure the rate of charging of a previously uncharged electroscope or electrometer, instead of observing the discharge rate, when working with the rays from a radioactive substance.   The principle involved in all these methods is the same, however ; it is always a question of determining the saturation current produced in a gas   Nevertheless, the theory of these methods will be more readily appreciated, if we introduce at this stage a short account of the conduction of electricity in gases.

5. CONDUCTION OF ELECTRICITY IN GASES

By way of illustration we shall proceed from the more generally familiar conduction of electricity in liquids. As detailed in every text-book of chemistry or physics, pure water is practically a non-conductor of electricity , but when we introduce an electrolyte such as hydrochloric acid into it, the liquid acquires the ability to conduct an electric current.   Moreover, it can be shown that at the same time there occurs a wandering of H-atoms towards the cathode, and of Cl-atoms towards the anode.   From this it follows that the H-atoms are positively charged, whereas the Cl-atoms possess a negative charge, and that the passage of the current consists in a transport of these charged particles.

Furthermore, we can readily calculate the magnitudes of the charge of these particles, which are called *ions* (" wanderers "). According to Faraday's Second Law, the same quantity of electricity is always necessary in order to deposit 1 gram-equivalent of a substance, this quantity amounting to 96,493 coulombs.   With this quantity of electricity we can, for instance, separate 1·008 gm. of

hydrogen or $\frac{16}{2} = 8$ gm. of oxygen. Now we know that $1 \cdot 008$ gm.
of hydrogen contains $6 \cdot 07 \cdot 10^{23}$ atoms, and hence every atom of
hydrogen bears a charge of $\dfrac{96493}{6 \cdot 07 \cdot 10^{23}} = 1 \cdot 59 \cdot 10^{-19}$ coulombs.   Such
small quantities of electricity are advantageously expressed in
terms of another system of units; since 1 coulomb $= 3 \cdot 10^9$ electro-
static units, it follows that the charge borne by a mono-valent
ion is $1 \cdot 59 \cdot 10^{-19} \times 3 \cdot 10^9 = 4 \cdot 77 \cdot 10^{-10}$ e.s.u.   A di-valent ion re-
quires 96,493 coulombs to deposit $\frac{1}{2}$ a gram-atom, and since this
$\frac{1}{2}$ gram-atom only contains half the number of atoms contained in a
gram-atom, we see that in this case each individual atom carries a
double charge $= 2 \times 4 \cdot 77 \cdot 10^{-10}$ e.s.u., and that every tri-valent ion
carries a treble charge, etc.

The fact that the charge of an ion is either $4 \cdot 77 \cdot 10^{-10}$ e.s.u.
or a whole multiple of that value, leads us to the atomistic conception
of electricity ; a smaller quantity of electricity than this " elementary
charge e " has never been observed.   As is well known, in the case
of these negative " quanta " of electricity it has been possible to
establish their independent existence, free from matter ; they
invariably possess the same electrical charge, independently of the
substance from which they were derived.   We shall meet with them
again in the β-rays from radioactive substances.

We shall use this well-known conception of the conduction of
electricity in liquids as a starting-point from which to render clear
the corresponding phenomenon in the case of gases, where the
following observations have been made.

Charged bodies that are in contact with a gas gradually lose their
charge.   Coulomb thought that the gas molecules become charged
by contact, and then hand over their charges to the walls of the
vessel.   However, this interpretation stands in contradiction to
the observation that the loss of charge is greater, the greater the
containing vessel.   From this we may conclude that the discharge
is accomplished by the aid of particles which are present in limited
number within the vessel, and which cannot be replaced after they
have been used up.   This conclusion is confirmed by experiments
with gases, the conductivity of which is greatly increased by allowing
them to bubble through water, by bringing them into contact with
flames, electric arcs, glowing metals or phosphorus, or by subjecting
them to the influence of ultraviolet light, cathode rays, positive rays,
Röntgen rays, or the rays from radium.   The enhanced conductivity

vanishes of its own accord in the course of time, but with especial rapidity when the gases are passed through glass wool, through narrow metal tubes, or through an electric field. Thus the conductivity must be attributed to particles that can be filtered from the gases and which are electrically charged. Since the gas as a whole shows no electric charge, an equal number of positive and negative particles must be present. These particles are also called " ions," and the production of conductivity is called the " ionisation of the gas."

Thus, just as in salt solutions, the conduction of electricity in gases is brought about by the agency of electrically charged particles. Nevertheless, there are important differences between the two phenomena. We have already had occasion to speak of one of them, namely, the relation between potential and current strength. As is well known, this relation is given within wide limits in the case of electrolytically conducting liquids by Ohm's Law, $I = V/R$, just as with metallic conductors, i.e. the current is proportional to the potential when the resistance is constant We explain this law by saying that with twice the potential the force acting on the ions is twice as, large, and hence the velocity they acquire in the resisting medium is also twice as large, so that the current or the quantity of electricity transported in the unit of time will also have double its previous value. This proportionality between current and potential can be graphically represented by means of a straight line passing through the origin. With gases ionised by Röntgen rays or the rays from radium, on the other hand, we have seen that this simple relation only maintains for the initial part of the curve (the region of Ohmic current, cf. Fig. 3), but when the potential is sufficiently high, the " saturation current " is attained, and this cannot under normal circumstances be exceeded. In this connection it is particularly striking that the saturation current is greater the farther apart are the electrode plates of the ionisation chamber, whereas with metallic conductors and electrolytes the current diminishes as the distance increases, owing to the increased resistance.

These results are explained in the following manner. Both in the case of electrolytic and of gaseous ions a fraction of the ions disappears by virtue of the recombination of ions to form neutral particles, even in the absence of an electric field. In the stationary state, a condition of dynamic equilibrium exists between the HCl molecules that are split up into ions in each second of time by the

dissociating action of the water, and the ions that reunite during the same interval to form uncharged molecules.   Likewise, a state of dynamic equilibrium is also maintained between the gas molecules that are broken up into ions by the action of the Röntgen rays, and the ions of the gas that combine to form uncharged particles.*

When an electric field is applied, the positive ions wander to the cathode and the negative ones to the anode, and if the field is of sufficient strength the transport may take place so quickly that the ions no longer have an opportunity of losing their charge by recombination, and they all give up their charge to the electrodes.   Now with electrolytes this case cannot be realised ; first, because the number of ions is very large, and secondly, because they can only be transported slowly towards the electrodes owing to the resistance offered by the water.   Thus, even when a strong field is applied the equilibrium between dissociation and recombination of the ions is not appreciably disturbed

On the other hand, in gases that are ionised by means of Röntgen rays or the rays from radium the number of ions is much smaller and their mobility much greater.†   In this case, by increasing the potential, it is actually possible to remove to the electrodes all the ions

* The velocity of recombination of oppositely charged ions to form uncharged particles is proportional to the product of the concentrations of the positive and negative ions.   Hence the number dn of the ions that combine per unit of volume in the time dt is given by the equation

$$\frac{dn}{dt} = a n_1 n_2$$

The constant a is called the *coefficient of recombination*   Since the same number of positive and negative ions are formed per unit of time, we have $n_1 = n_2$, and the above equation becomes

$$\frac{dn}{dt} = a n^2.$$

† Whereas the ion content in a strongly dissociated normal solution of an electrolyte amounts to about 10^{20} per cc., it rarely exceeds 10^8 per cc. in a gas, even with the strongest ionisation by Röntgen rays or the like.   The mobility of ordinary gas ions in oxygen is about 1 to 2 cm./sec per volt/cm., and in hydrogen it even reaches the value of 7 to 8, whereas the mobility of most electrolytic ions (Cl, K, etc.) in water only amounts to $7 . 10^{-4}$, and even that of the H-ion does not exceed $3 \cdot 10^{-3}$.   Both factors, namely, the smaller number and the greater mobility of the ions, are favourable to the attainment of the saturation current in the case of gases.   The conductivity is reduced by the first factor, and increased by the second, but in a much lesser degree, so that the conductivity even in hydrogen can only reach a value corresponding to that of an acid solution of strength about 10^{-10} N.

produced during a definite time by the action of the ionising agent, or, in other words, all the ions take part in the transport of the current. As soon as this condition is fulfilled, a further increase of the potential difference is no longer able to bring about an increase in the current, for of course only a definite number of ions is being produced per unit of time. If the ionising action is increased, the value of the current will also rise, since there are now more ions available. Thus the current is now a measure of the ionising action, and, within certain limits, it is independent of the potential. Hence, if we desire to measure exactly the ionising action of a preparation, it is necessary to make use of the saturation current

The first part of the curves in Fig 3, the region of Ohmic current, completely corresponds to the conditions with electrolytes, but the remainder of the curves (incomplete saturation and the saturation current) is not attainable in the case of electrolytes.

The explanation of the above-mentioned phenomenon, viz. that the saturation current becomes greater when the plates are farther apart, is also given directly by the theory. If the ionisation takes place uniformly throughout the gas, the number of particles produced, per unit of time between the electrodes will be greater the greater the distance between the plates, and hence the current may also be larger.

In view of its practical importance, we have dealt in some detail with the dependence of conductivity on the potential. But there are still other important differences between electrolytic ions and gas ions. In the first place, with the latter ions the close relationship of the charge and the chemical nature is absent It is well known that in electrolysis hydrogen always carries one positive charge, and oxygen always carries two negative charges, etc. ; but the gas ions in hydrogen and oxygen carry exactly the same charges. Moreover, whilst we meet with ionised atoms in the solutions of most substances, the gas ions of the same substance generally consist of ionised molecules. In electrolysis all the ions have similar dimensions, even though, in consequence of stronger or weaker hydration, somewhat considerable differences in their magnitude (and corresponding mobility) occur , in the case of gas ions the multiplicity is much greater, and at the present time we can visualise the following picture of the process of ionisation in gases.

As a result of the collisions of gas molecules and the electrons of cathode or β-rays (or even secondary electrons that have been

produced by Röntgen rays, γ-rays, or ultraviolet light), a neutral particle parts with an electron. Thereby a positive ion of atomic dimensions is produced simultaneously. At low pressure or at high temperature these ions exist as free ions in the gas, but otherwise uncharged particles attach themselves to the ions by virtue of electrostatic attraction, and thus increase the mass of the ions. It has been calculated from diffusion measurements that ordinary gas ions (" small ions " or " molecular ions ") generally consist of a cluster of about thirty molecules. The charge is independent of the number of associated particles ; it may remain a single elementary charge, but further charged ions may attach themselves. Apart from electrons, positive atomic ions, and positive or negative molecular ions, there also exist " large ions " (also called " slow ions "). These deserve mention because they are sometimes present at the commencement of ionisation measurements, when they hinder the attainment of the saturation current.

In contrast to the case of electrolytic ions, we must, with gas ions, assume an important difference between positive and negative ions ; the positive ones are always associated with a mass of the order of magnitude of that of an atom, but the negative ions sometimes occur in the form of electrons, particularly when the pressure of the gas is low.

This has an important bearing in connection with the ionisation of gases by collision. We have already seen that when the gas in an ionisation chamber is ionised, the form of the curve between current and potential is represented by Fig. 3, the current remaining constant after a certain value of the potential has been attained. But the value of the current does not remain constant indefinitely as we increase the potential on the plates, and at normal pressure a spark ultimately passes between them. If the same experiment be performed with the gas at a reduced pressure of a few centimetres of mercury, we are readily able to determine the exact form of the characteristic curve for the gas, up to the point where a luminous discharge takes place. At first it is as in Fig. 3 ; but when a certain critical voltage has been reached, the current again begins to increase, slowly at first, then with increasing rapidity until a glow discharge is initiated. The value of the critical voltage depends on the pressure, being less for lower pressures. This renewed increase in the current after the critical voltage has been reached is due to the fact that the ions acquire sufficient energy in the electric field to produce further

ions by their collision with the molecules of the gas. As the pressure in an ionised gas is diminished, the proportion of negative ions in the form of electrons increases, and it is these ions which at first give rise to the growth of current when the critical voltage is attained ; later, however, the positive ions also participate. In this manner it is possible to maintain a current of, say, one thousand times the value of the saturation current, by virtue of the ions formed by collision.

Perhaps the most important application of this phenomenon in radioactivity has to do with the counting of the rays emitted by radium and other radioactive substances. In a form frequently used, the counter consists of a metal hemisphere of, say, 2 cm. diameter, at the centre of which is situated a small metal sphere of from 4 to 5 mm. diameter, soldered to a rod passing through the insulating plug which closes the hemisphere This rod is connected to a fibre electrometer. A small hole in the front of the counter serves to admit the corpuscular rays, the hole being closed by a thin mica window. When the pressure of air within the counter is about 4 cm and the hemisphere has a positive potential of about 1400 to 1600 volts, the ionisation caused by the entry of an α-particle is multiplied sufficiently to be detectable as a sudden kick of the electrometer fibre. By counting the kicks, the number of α-particles entering the counter is evaluated. Sometimes the counter is cylindrical in shape, and the central sphere is replaced by a needle point. This method is briefly referred to in the following chapter, and possesses the advantage that it can be worked at normal atmospheric pressure. Both forms of counter also react to the entrance of β- and γ-rays.

II

THE α-RAYS

1. MASS AND CHARGE OF THE *a*-RAYS

As already mentioned, it follows from the direction of the deflection experienced by *a*-rays in a magnetic field that they consist of positively charged particles. But an electric field also deflects them. If we combine the magnitudes of the electric and magnetic deflections, we obtain a quantity which is always very characteristic for charged particles, viz. the ratio of the charge to the mass of the particle, or the specific charge, e/m. We shall consider as the unit of charge the elementary charge of electricity, *i.e.* that of a mono-valent ion ($e = 4.77 \cdot 10^{-10}$ e.s.u.), and as the unit of mass the mass of a hydrogen atom ($m = 1 \cdot 66 \cdot 10^{-24}$ gm.). In terms of these units we obtain for e/m in the case of *a*-particles the value $\frac{1}{2}$, *i.e.* such a particle carries either a single elementary charge and has an atomic weight $= 2$, or it carries two elementary charges and possesses an atomic weight $= 4$, etc. We are able to decide between these alternatives both by physical and by chemical methods.

A luminescent screen, *e.g.* a surface coated with zinc sulphide, is caused to emit a flash of light by the incidence of every single *a*-particle upon it. If we count these *scintillations*, and determine in addition how much positive electricity is conveyed to an electrometer from the same source of *a*-rays under identical conditions, we obtain the amount of charge carried by a single particle by dividing the second number by the first (*1*). The result is found to be two elementary units. From this it follows that the mass of the particle has the value 4, the atomic weight of helium.

• This result is confirmed by the following chemical experiment. If we introduce radium emanation or some other *a*-rayer into a glass tube with thin walls ($< \frac{1}{100}$ mm. thick) and seal it off, it is found that the *a*-particles pass through the tube. But if this tube be now enclosed in a wider evacuated tube with sealed-off ends and thick walls, we are no longer able to detect *a*-particles outside the tube. Hence the particles must have been retained in the space between the

glass tubes or in the walls of the outer one. As a matter of fact, it has been found possible to detect the appearance of helium in the intermediate evacuated space by spectroscopic means (cf. experiment (5) on p. 2). The amount of helium produced by 1 gm. of radium in one year has the value 167 mm.[3]

We are thus led to the conclusion that α-particles are helium atoms with which are associated two positive elementary charges.

If α-rays are produced during a radioactive transformation, then the process proceeds in such a manner that each disintegrating atom gives rise to one, and only one α-particle. This important fact was established by means of counting experiments, in which the number of the atoms disintegrating in a given time was known, and the number of α-particles emitted in the same time was determined by the optical method already referred to, or by an electrical method. One of the best known electrical methods is based on the fact that a momentary brush discharge always occurs from a highly charged needle point when a passing α-particle ionises the air in the immediate proximity of the point. The number of these brush discharges can be registered by means of an electrometer.

The number of α-particles emitted per second by 1 gm. of radium (free from its products of disintegration) has the value $3·72 \cdot 10^{10}$, and when the radium is in equilibrium * with three of its disintegration products that emit α-rays, the number has four times this magnitude (2). From this we can calculate how many helium atoms must be contained in the 167 mm.[3] of helium that are produced from 1 gm. of radium in the course of a year. This number of helium atoms is obviously $3·72 \cdot 10^{10} \times 4 \times 365 \times 86400 = 4·58 \cdot 10^{18}$. According to the value of Loschmidt's number, which is obtained in quite a different manner, there must be present in 1 cc. of every gas $2·71 \cdot 10^{19}$ particles (molecules), so that theoretically we should expect 167 mm.[3] of helium to contain $2·71 \cdot 10^{19} \times 0·167 = 4·53 \cdot 10^{18}$ atoms. This excellent agreement offers convincing proof of the correctness of the atomistic conception of matter, for in the example just given it has been possible literally to count the number of atoms which occupy a definite volume of a gas

2. ABSORPTION, RANGE, AND VELOCITY OF THE α-RAYS

If we bring a preparation which emits α-rays, *e.g.* a surface coated with polonium, near a zinc sulphide screen, the latter is found to

* For the meaning of the term "radioactive equilibrium," see p. 86 ff.

become luminescent under the action of the rays. On gradually removing the preparation, the luminescence of the screen suddenly ceases at a distance of the radioactive film from the screen, which has in this case the value 3·93 cm. (at 15° C.). At the same distance, the ionising * and all other actions of the rays also disappear. (Cf., however, p. 25.)

The existence of a sharply defined limit beyond which no further ionisation takes place is a most characteristic property of the α-rays. The determination of this *range* can be performed with great accuracy by a variety of methods   (Cf. p. 78.)

In Table I are collected together the ranges for the radio-elements emitting α-rays, as determined in air at normal atmospheric pressure and 15° C. (*3*). When not otherwise stated, range determinations are always referred to these conditions of pressure and temperature. Hitherto, the longest known range was that of ThC', but it has been recently established that $\frac{1}{11,000}$ of the α-particles from a preparation of ThC have a range of 11·3 cm. (*4*). (See Fig. 27.) For reference in connection with the following section, the number of pairs of ions produced by each type of α-ray in its track is given in column 4 of Table I

The range is inversely proportional to the pressure of the gas, and directly proportional to the absolute temperature. Hence α-rays exhibit very large ranges in a high vacuum. Furthermore, the range is proportional to the cube of the velocity of the α-particle. The velocity, and hence the range of an α-particle, can be influenced by the application of a strong longitudinal electric field. Thus the effect of a potential difference of 10,000 volts was to modify the range of the α-particles from RaF in air by 0·0226 cm. (*5*).

Owing to the much larger densities of liquids and solids, the range of α-particles in them is much smaller than in gases. The α-rays of a uranium preparation are absorbed by a sheet of aluminium of thickness 0·022 mm., and those of ThC' by a sheet of aluminium 0·065 mm. thick   Accurate range determinations in liquids and in solids are much more difficult to carry out than in gases, but even with them reliable values have been obtained by

* If we introduce the radioactive film into an α-ray electroscope, the two plates of the ionisation chamber being separated by considerably more than 3 93 cm., we still find that the preparation produces an effect on the electroscope. Diffusion and transport of the ions of air in the electric field result in their gaining admittance to the whole of the intervening space before recombination occurs, and hence the electroscope loses its charge.

TABLE I

Ranges and Initial Velocities of α-Rays at 15° C. and Atmospheric Pressure

Substance	Range in cm	Velocity in cm./sec.	Number of pairs of Ions per α-particle.
Uranium I - - -	2·83	$1·423 . 10^9$	$1·28 . 10^5$
Uranium II - - -	2·91	1·437	1·32
Ionium - - -	3·194	1·482	1·46
Radium - - -	3·389	1·511	1·52
Radium Emanation -	4·122	1·613	1·71
Radium A - - -	4·722	1·688	1·87
Radium C′ - -	6 971	1·922	2·37
Radium F (6) - -	3·925	1·587	1·67
Protactinium - - -	3·673	1·552	1·60
Radioactinium -	4·676	1·682	1·87
Actinium X - - -	4 369	1·645	1·78
Actinium Emanation -	5 789	1 807	2 11
Actinium A - - -	6 584	1·886	2·28
Actinium C - - -	5·511	1·777	2 05
Thorium - - -	2·90	1·435	1·37
Radiothorium - -	4·019	1·600	1·69
Thorium X - - -	4·354	1 643	1·77
Thorium Emanation -	5·063	1 728	1 95
Thorium A - - -	5 683	1·796	2 09
Thorium C - - -	4 787	1·696	1 89
Thorium C′ - - -	8·617	2·063	2 74

special methods (7).   For example, Table II contains the values of the ranges of the α-particles of RaC in several solid elements.

TABLE II

Range of the α-Particles from RaC in different Metals

Metal	Range	Metal.	Range	Metal	Range.
Li	129μ	Cd	$24·2\mu$	Fe	$18·7\mu$
Ca	78·8	Pb	24·1	Ni	18·4
Mg	57·8	Tl	23·3	Cu	18·3
Al	40·6	Zn	22·8	Au	14·0
Sn	29·4	Ag	19·2	Pt	12 8

It is seen that the range diminishes as the density of the material increases.   In water, the range of the rays from RaC has the value $60·0\mu$, and 50μ in the sensitive film of a photographic plate (8).

For the purpose of practical measurements a medium can also be conveniently characterised by the statement of its *air-equivalent*, instead of by the range. This term refers to the thickness of a layer of air which would reduce the range of an *a*-ray by just the same amount as the medium in question. Mica, for example (density 2·87), in the form of a thin sheet of such thickness that it weighs 1·50 mgm. per sq. cm., has an air equivalent of 1·0 cm. (at 760 mm. and 15° C.) (*9*). If we extrapolate for thicknesses which would correspond to the whole range in air, the air equivalent as above determined does not always give the correct range of the *a*-rays in the substance concerned. This is due to the fact that air equivalents themselves are dependent on the velocity of the rays, and hence one and the same sheet, introduced at different points of the trajectory, shortens the range in air by different amounts.

In the investigation of the behaviour of different media with respect to the same *a*-rays, we often take account of the *stopping power*, instead of the range or the air equivalent. The stopping power of a medium is the quantity that expresses how many atoms of a standard substance are equivalent to an atom of that medium as regards absorption. Air is usually chosen as the standard substance. What has been said of the air equivalent holds here also, but the idea of stopping power becomes unequivocal as soon as we speak of the *average stopping power*, *e.g.* when we understand by the stopping power of aluminium for the *a*-rays of RaC that quantity which expresses how many " atoms " of air an aluminium atom is able to replace *on an average* throughout the whole of their path. The retardation of the *a*-rays in their passage near to or through an atom is due to the fact that the *a*-particle transmits energy to the atom, in which process the electrons in the atom take up orbits of higher energy content, or may be entirely separated from the atom (ionisation). The stopping power must accordingly be determined by the number of electrons in the atom, as well as by the frequency of the motions which these electrons carry out in their normal orbits (*10*).

Considering only the first of these two causes, we must expect that the stopping power will increase with the ordinal number * of the element, which is always equal to the number of electrons in the atom. Moreover, since the atomic weight practically always

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* * For a more detailed explanation of the expression " ordinal number," refer in particular to Chapter XVI.

becomes greater with increasing ordinal number, we should also expect an increase in the stopping power (*11*) with increasing atomic weight, and as a matter of fact this is what occurs, as is shown by the figures in Table III. We also see that the ratio of the stopping power (*s*) and the square root of the atomic weight (*A*) is fairly constant. Still greater constancy is shown by the ratio of the stopping power and the $\frac{2}{3}$ power of the atomic or ordinal number (*N*), whereas the ratio *s*/*N* is not so constant (*12*).

TABLE III

Stopping Power of different Atoms towards α-Rays

Substance	Stopping Power *s*	$s/\sqrt{A}$	$s/N^{\frac{2}{3}}$
H	0·20	0 200	0·200
C	0·85	0·246	0·255
O	1·05	0 262	0·261
Al	1·495	0·287	0·271
S	1·76	0·312	0 277
Fe	2·29	0 307	0·261
Ag	3·28	0 316	0·252
Pt	4·14	0 297	0 227
Au	4·22	0 301	0 229
Pb	4 27	0·298	0 226

The stopping power of a molecule is derived additively from those of its constituent atoms. but this relation is not strictly valid (*13*). Considerable deviations from the additive law are found in the case of the lightest of the elements : thus from the stopping power of the H_2-molecule we obtain for the H-atom the value $s = 0\cdot200$, whereas the compounds C_2H_4, C_2H_6, CH_4 (using the value of C for diamond) yield the value 0·187, and from NH_3 we obtain the value 0·173. For CO_2 and CO the additive law was found to have strict validity. As applied to α-rays of different range, the stopping power of atoms shows only approximate constancy. It increases with increasing range when the atomic weight of the absorbing substance is greater than the mean atomic weight of air (14·4), and it diminishes with increasing range in the reverse case. The absorbing action of a compounded sheet, consisting of layers of two different materials, is for this reason dependent on which side of the sheet is facing the source of radiation. An exact calculation of the stopping power in terms of universal constants is possible in those cases for

which the velocity of the revolving electrons in their stationary orbits
is small compared with the velocity of the incident α-rays.   Calcula-
tion is in accord with experiment, for instance, in the case of the
lithium atom, the stopping power of which is twice that of an atom
of hydrogen.

In their passage through matter, α-rays suffer a very considerable
diminution in velocity, in consequence of which the phenomenon
described above arises, viz. that the α-rays soon lose their character-
istic properties (excitation of fluorescence, blackening of a photo-
graphic plate, ability to ionise), and thus reach the end of their range.
If we disregard the very last part of the track of an α-particle (14),
a simple relation is found to exist between the velocity and the
range of the particles.   At any point of the track, the distance
remaining to be traversed is proportional to the third power of the
velocity at that point.   According to this relation we can thus
calculate the initial velocity of the α-rays from RaA, which we find
to be $1 \cdot 693 \quad 10^9$ cm./sec., whereas from experiments on the magnetic
and electric deflection of the rays the value $1 \cdot 692 \cdot 10^9$ cm./sec. is
obtained (15).   The velocity of the α-rays from polonium amounts
to 0·829 that of RaC', which has the value $1 \cdot 922 \cdot 10^9$ cm./sec , and
it is found that the velocities of the individual α-particles emitted
by polonium differ by less than 0·3 % (16).   For purposes of com-
parison it is interesting to mention that positive rays with a velocity
of $2 \cdot 7 \cdot 10^8$ cm /sec. are able to ionise through a distance in air of
about 1 mm

α-rays with a velocity of less than about 0·01 of the velocity of
light cannot then be detected by the scintillation method.   Pre-
sumably they become neutral atoms of helium at such small velo-
cities, by each taking up two electrons.   By means of experiments
on their photographic action in a magnetic field, and by scintillation
experiments in a magnetic field, we are able further to conclude
that an appreciable fraction of the α-particles has already taken up
one electron per α-particle. even when the velocity has only diminished
to the equivalent of 800,000 volts (17), and that an α-particle
successively captures and loses an electron several hundred times
before it reaches the end of its track   If a pencil of α-rays be passed
through a thin metal sheet, it is found that, according to the velocity
of the rays, there is in the transmitted pencil a definite ratio
$He^{++} : He^+$ (α-particles : singly positively charged atoms of He), and
uncharged helium particles (neutral atoms of helium) can also be

detected in the pencil of rays (18), the latter having sufficient velocity to produce scintillations.

From a study of the curvature of α-ray cloud-tracks in a very strong magnetic field (75,000 gauss), it has been found that the average charge on α-particles 8 mm from the end of their range is 1·5e, and that it is less than e at a distance of 3 mm from the end of the range (19). α-rays with a velocity even less than 0·01 that of light can be rendered visible by the cloud-track method (cf. p. 78), the minimum effective velocity being about $\frac{1}{4}$ of that value, and corresponding to $\frac{1}{2\cdot 3}$ of the initial velocity of the rays from RaC'. The kinetic energy of α-particles with this velocity is still appreciably greater than that of an electron which has fallen through a potential difference of 13·5 volts, but in view of the fact that α-particles lose their charge for velocities of this order. we should not expect them to produce many pairs of ions when their velocity has diminished below the value mentioned.

3 THE IONISATION PRODUCED BY α-RAYS

In consequence of its large velocity, an α-particle possesses a very considerable kinetic energy amounting to about 10^{-5} ergs at the beginning of its path, or roughly 10^{11} times the value of the thermal energy of a helium atom at room temperature By virtue of this kinetic energy, the α-rays give rise to strong ionisation along their path by their collisions with gas molecules (20). Thus an α-particle of RaC' produces along its track of length 6·94 cm in air at atmospheric pressure and 0° C. no fewer than 2·37 . 10^5 pairs of ions (i.e. equal numbers of positive and negative ions). The
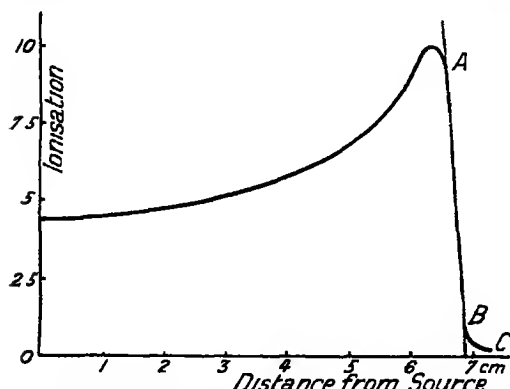
FIG 7   Variation of the Ionisation produced by an α-Particle with Increase of Distance from the Source

total number (k) of pairs of ions (21) produced by an arbitrary α-particle amounts to

$$k = k_0 . R^{\frac{2}{3}},$$

where k_0 is a constant $= 6·76 . 10^4$, and R signifies the range (see Table I).

The intensity of ionisation of the α-particles emitted by RaC in air, in its dependence on the distance from the source of rays, is represented in Fig. 7. It is seen that quite near to the end of the track the ionisation increases considerably, and then diminishes very rapidly (22). The last part (BC) of the graph shows a slight tailing off, probably as a result of scattering. Since in consequence of this the range cannot be obtained from the graph with sufficient precision, it is customary to produce the rectilinear part (AB) of the graph until it cuts the abscissa, and to consider the distance of this point of intersection from the origin as the range.

If several α-rayers are simultaneously present in the source, the curve of ionisation has a more complicated form. Fig. 8 shows the ionisation curve of the "active deposit" (see p. 89) of thorium. The occurrence of such a curve always indicates the presence of a hetero-geneous radiation, or, since each α-transforma-tion is accompanied by a homogeneous radi-ation, bears witness of the presence of different
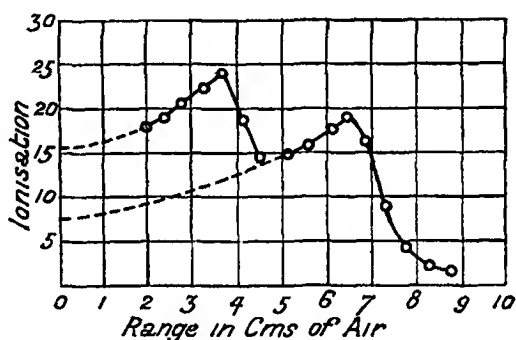
Fig 8　Curve of Ionisation due to Presence of two α Rayers
(ThC and ThC)

products emitting α-rays. Just as an analysis of the curves representing the variation of activity with time (see Ch VIII) renders possible the interpretation of the process of disintegration, so we can also make use of an analysis of the curve of ionisation for this purpose. Thus Fig. 8 shows that there are two α-rayers in the active deposit of thorium, namely ThC and ThC', with ranges of 4·80 and 8·62 cm. respectively.

When a parent substance is in equilibrium with several dis-integration products (see p. 96 ff.), the part played by the individual disintegration products in building up the total ionisation depends not only on the number, but also on the ranges of the individual α-rays. Thus the ratio of the ionisation produced by

$$ThX + ThEm + ThA + ThC$$
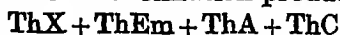
to that produced by RdTh is only 3·66, whereas that of the ionisa-tion of RaEm + RaA + RaC to the ionisation of Ra is 4·11.

Since the energy necessary to produce a pair of ions depends on

the nature of the gas, there exist between the values of the total
ionisation produced by an α-particle in different gases differences
of varying magnitude, according to the velocity of the α-rays used.
Thus for α-rays from polonium of residual range 7 mm. we find the
following relative values of the total ionisation (23). In diatomic
gases the ionisation is less than in any of the monatomic gases.
Most of the ions produced possess a single electronic charge. Thus
in the ionisation of H, C, O, N. Cl, I, and Hg, presumably only 5 ions
in 2900 carry a double charge. On the other hand, it has been found
that in helium about 10 % of the ions observed are doubly charged
(24).

<div align="center">TABLE IV</div>

Relative Ionisation of the α-Rays from Polonium in different Gases

Air	-	-	-	-	-	1
Helium	-	-	-	-	-	1·26
Neon	-	-	-	-	-	1·28
Argon	-	-	-	-	-	1·38
Nitrogen	-	-	-	-	-	0·98
Oxygen	-	-	-	-	-	1·08

4. SCATTERING OF α-RAYS

If we allow the α-particles from a point source to pass in a narrow
pencil through thin metal foils *e.g* through a gold sheet of thickness
$\frac{1}{100}$ mm., and then to fall on a scintillation screen held in different
positions and in such a manner that the normal through its mid-point
passes through the point at which the rays are incident on the foil,
making different angles with the direction of incidence of the rays,
we find that a fraction of the α-rays is deflected through a small
angle from their original direction. Some of the particles are
scattered through a considerable angle, and a very small number
suffer a deflection of nearly 180°, and can be detected on the screen.
Thus it was found that when RaC was used as source one particle in
8000 was deflected through more than 90° in the passage of the rays
through thin platinum foil

The so-called scattering coefficient ϕ—*i.e.* the most probable
angle of deflection for a sheet of such thickness that its air-equivalent
is 1 cm.—is dependent on the material of the foil, and in the case of
the α-rays from RaC it has the following values :

Au.	Ag.	Cu.	Al.
$\phi = 2\cdot1°$	1·5°	·1·1°	0·6°

Since experiments have shown that the deflection caused by an atom is roughly proportional to the weight of the atom, it follows that the phenomenon of scattering is detectable chiefly in the case of the passage of the rays through heavy atoms. ϕ increases, moreover, as the velocity of the α-particles diminishes, and is inversely proportional to the second or third power of the velocity. So long as the thickness of the scattering layer remains small, the angle of deflection undergoes an increase proportional to it

The scattering of α-particles can also be established by photographic means. For this purpose the source of the rays is laid on the photographic film, and after development the tracks of the particles are seen as a series of radial lines of blackened points (*i.e.* silver bromide particles that have been struck by α-particles), and some of these show sudden bends, sometimes through large angles (*25*). Experiments in gases saturated with water vapour also show the phenomenon of scattering very clearly (see p 78) Scattering plays an important part in the investigation of the constitution of atoms, and we shall discuss it further in that connection. At this juncture it will suffice to mention that, from the ratio of the number of α-particles that are deflected through an angle ϕ from the original direction of the rays to the number falling on an equal area in the same time when no scattering sheet intervenes, it is possible to calculate the nuclear charge number for the scattering element. The mean value of various observations in the case of platinum was 77·4, whereas the correct value is 78 (see p. 128) , the corresponding figures for silver are 46·3 and 47, and for copper 29·3 and 29 (*26*).

5. Probability Fluctuations in the Emission of α-Rays

If we count the number of scintillations produced on a scintillation screen by a constant and homogeneous source of radiation in intervals of, say, 15 secs. duration, we find that the values fluctuate ; in some cases they are larger, in others smaller than the average value. By average value we mean the number which results when the number of scintillations counted in, say, two hours is divided by 480 (*i.e.* the number of 15 second intervals in two hours) (*27*). The smaller the intervals are during which counts are made, the greater are the fluctuations obtained. This phenomenon represents a particularly simple example of probability fluctuations, the presence of which is always required by the statistical interpretation of natural

phenomena, when the quantities we observe are only average values. The abscissae of Fig. 9 show the numbers of α-particles counted in 15 sec. intervals, whereas the ordinates represent the number of experiments of that duration in which the above-mentioned numbers
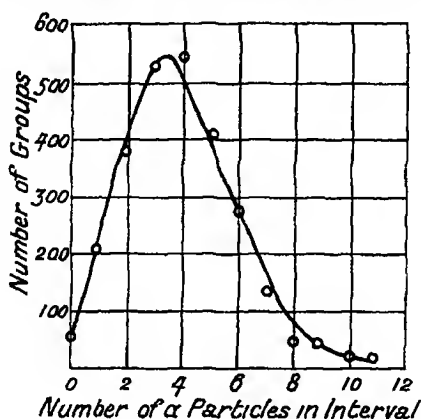
FIG. 9.   Fluctuations in the Rate of Emission of α-Particles

of particles were recorded   The results are in accord with those found from the calculus of probabilities.*   As in the emission of α-particles, we can also detect a probability fluctuation in the measurement of their ranges.

If we count the number of α-particles in a parallel pencil of rays at different distances from the source, by interposing a scintillation screen, we find the number remains constant until a point about 4-6 mm. from the end of the range is reached, when the number falls off more and more rapidly until the end of the range is reached. Within the last mm. of the range the diminution in the number of α-particles follows an exponential law, in accordance with theory. The former straggling process, however, is not explained by scattering effects, but the phenomenon of gain and loss of electrons by an α-particle near the end of its range is ample to account for this excessive straggling, since the penetrating power of a singly charged particle is considerably less than that of a doubly charged α-particle (28).

* If a represents the mean value, then the probability (p) that n particles will be emitted in a given interval of time is given by

$$p = \frac{a^n}{n!} \cdot e^{-n}.$$

III

THE β-RAYS

1. MASS AND CHARGE OF β-RAYS

THE deflection to which β-rays are subject when they pass between the poles of a magnet or between the plates of a charged condenser shows a great similarity in direction and in magnitude to that experienced by cathode rays. It has been shown by deflection experiments in a magnetic field that, just as the cathode rays possess different velocities according to the manner of their production, so also in the investigation of the β-rays from radioactive substances we find rays of different velocity. Here, however, we make the acquaintance of velocities of magnitude much greater than are ever reached by cathode rays; e.g. for RaC there are rays with a velocity equal to 0·998 of the velocity of light. In accordance with the theory of relativity, the mass of a body is dependent on its velocity of translation. In practice, this dependence does not become manifest until the velocity is very considerable, i e. of the order of magnitude of the velocity of propagation of light.* Thus, in the case of β-rays of large velocity, we are led to expect a marked dependence of the mass of a β-particle on its velocity, and this has been found to be in complete accord with the demands of the theory of relativity. Correspondingly, we differentiate between the so-called stationary mass and the translational mass of β-particles. For the former the same value was found as for the stationary mass of a cathode ray particle, viz. 0 898 .10⁻²⁷ gm , which corresponds to $_1\cdot_{1}^{1}_{4}$ of the mass of an atom of hydrogen. Thus we conclude that β-rays consist of quickly moving electrons

When β-rays fall on a positively charged electrometer, they

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* The mass m corresponding to the velocity v is given by

$$m = m_0 \cdot \left[1 - \left(\frac{v}{c} \right)^2 \right]^{-\frac{1}{2}}$$

where m_0 = the stationary mass, c = the velocity of light. Whereas particles with a velocity $\frac{1}{10}$ that of light only show an increase in mass $\frac{1}{2}$ % greater than that of the particles at rest, the value of m for particles with 0 998 of the velocity of light is 15 8 times the value of m_0.

discharge it ; conversely, a preparation emitting β-rays becomes positively charged when it is insulated, as can be shown by connecting it to an electrometer.   By exercising great care as to the insulation, it is possible in this manner with radium preparations to attain a charge corresponding to a voltage of 150,000 volts (see also " radium clock," p. 211).   It is possible to determine the *number of β-particles emitted* by a known quantity of radium, by noting the charge acquired by an electrometer to which it is connected, in consequence of the escape of β-particles.   This number can also be evaluated by allowing the rays to pass near a highly charged needle point, since each particle ionises the gas surrounding the point. Under these circumstances, the number of point discharges, which is equal to the number of particles, is conveniently registered by means of a suitable electrometer, *e.g.* a string (or fibre) electrometer (*1*).

In the case of α-transformations we saw that one atom emits but one α-particle, and it is found that in the transformation of a β-rayer such as RaB, RaC, or RaE (*2*), each disintegrating atom emits only one β-particle.   Thus 7.10^{10} β-particles are emitted in each second from the combined amounts of RaB and RaC in equilibrium with 1 gm. of radium (see p. 20).   The simplicity of the conditions maintaining in such experiments is very much masked by the occurrence of the so-called secondary rays, and we shall discuss them when we come to deal with secondary rays.

2 ABSORPTION AND VELOCITY OF β-RAYS

Corresponding to their large velocity, the penetrating power of most β-rays is considerably greater than that of α-rays.   In their passage through matter, the intensity of the rays gradually diminishes and the thickness of the layer by which they are *completely* absorbed depends in no small degree on the sensitiveness of our absorption measurements, in addition to the hardness of the rays.

For instance, if in the investigation of the β-radiation from RaE we plot as abscissa the thickness of the absorbing sheet of aluminium, and as ordinate the ionisation produced by the radiation, we obtain a simple regular graph.   The values of the ordinates diminish in geometric progression as the abscissae increase in arithmetic progression *   The intensity of the radiation is reduced to half its

* The decrease in the radioactivity of every simple disintegrating radioactive substance takes place according to the same type of curve (see graph *B* in Fig. 28. p. 85).

value in its passage through a layer of 0·16 mm. thickness, and after passing through $2 \times 0·16$ mm. it is reduced to a quarter, and so on. Accordingly, the *half-value thickness* of aluminium for the β-rays from RaE has the value 0·16 mm. The steeper the downward slope of the above-mentioned absorption curve, the more easily are the rays absorbed, and the smaller is the value of the half-value thickness. Instead of the last named quantity, we often consider the so-called absorption coefficient, which is equal to $\dfrac{0·693}{\text{Half-value thickness}}$, and usually designated by μ.*

The curves of absorption do not always show the simple form just described, which can be represented mathematically by means of a single absorption coefficient , in order to interpret them. it is often necessary to assume the existence of a mixture of rays, i e. different absorption coefficients. Thus the β-rays from RaB exhibit the absorption coefficients 13, 77, 890 when they are passed through aluminium. The absorption coefficients of different β-rays in aluminium are given in Table V

<p style="text-align:center">TABLE V</p>

<p style="text-align:center">Absorption Coefficients of Different β-Rays</p>

Radio-element	Absorption Coefficient (μ) in Aluminium
UX_1	460
UX_2	18
Ra	312
RaB	13, 80, 890
RaC	13, 53
RaD	5550
RaE	43

When the absorption coefficient is small, the half-value thickness is large, *i.e.* the penetrating power is large , for this reason such rays are also called "hard," in contradistinction to the easily absorbed "soft" rays.

* If I_0 is the intensity before absorption, and I the intensity after the passage of the rays through a layer of thickness d, then $I = I_0 . e^{-\mu d}$, where $\mu =$ the absorption coefficient. Putting $I = \dfrac{I_0}{2}$, we find $\mu = \dfrac{\log_e 2}{d} = \dfrac{0 693}{d}$ cm.$^{-1}$. Thus the *half-value thickness* is related to the *absorption coefficient* in the same way as the *half-value period* to the *disintegration constant*. (Cf. p. 82.)

If we investigate the absorption of one and the same β-radiation in different materials, we find that the absorption coefficient increases with the density of the absorber, but that the ratio of the two quantities is not strictly constant. Table VI contains a number of values of the ratio of the absorption coefficient to the density for

TABLE VI

Ratio of the Coefficient of Absorption to the Density of the Absorber

Substance	Density	$\dfrac{\text{Absorption Coefficient}}{\text{Density}}$
Carbon - - -	1 8	4·4
Sulphur - - -	2 0	6·6
Boron - - -	2 4	4·65
Aluminium - -	2 7	5·26
Barium - - -	3 8	8·8
Iodine - - -	4·9	10·8
Tin - - -	7 3	9·46
Copper - - -	8 9	6 8
Lead - - -	11·3	10 8
Gold - - -	19 3	9 5

a variety of solid elements and for the β-rays from UX_2, whereas Table VII gives a comparison of the absorption coefficients of β-rays of varying hardness in air and in carbon dioxide

TABLE VII

Coefficients of Absorption of Different β-Rays (3) in Air and Carbon Dioxide (at 1 Atmos and 22° C), arranged in decreasing order of hardness of the β-rays (4)

Radio-element	Air	Carbon Dioxide
ThC' + ThC"	0·0068	0 0129
RaE	0 0152	0 0297
ThB	0 090	0 142
UX_1	0 12	0 23
RaD	0 64	1 69

The absorbing power of a chemical compound is built up additively from those of its elementary constituents.

PLATE I

FIG 10 (p 35)
Magnetic β-Spectrum of the Members of the Actinium Series (Rd Ac, AcX, AcB, and AcC)

3,2   1,4   0,7   0

50   20   10   6,4

$\times 10^{-4} cm\ Al$
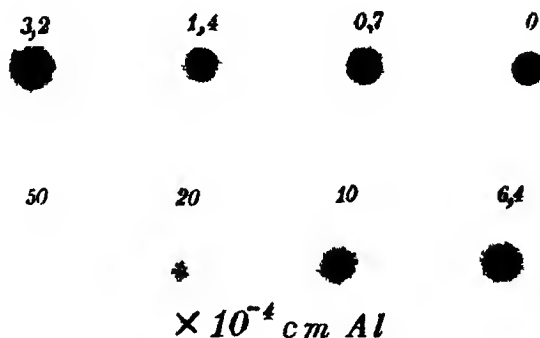
FIG 13 (p 39)
Scattering of β-Rays after passing through Aluminium Foil

Hf Lα₂
Hf Lα₁
Cu Kα₂
Cu Kα₁
Hf Ln
W Lα₂
W Lα₁
Hf β₄ Cu Kβ₁
Hf Lβ₁
Hf Lβ₃
Hf Lβ₂
W Lβ₁
W Lβ₂
Hf Lγ₅
Hf Lγ₁
Hf Lγ₂
Hf Lγ₃
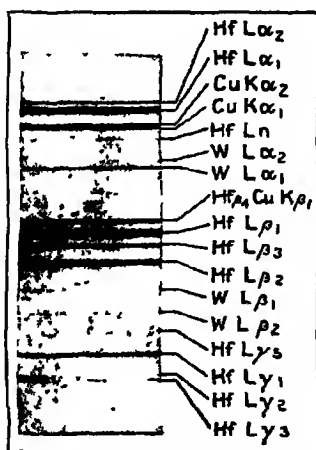
FIG 14 (p 54)
L-Spectrum of Hafnium

The exponential form of the absorption curves does not always prove the homogeneity of the radiation corresponding to them, for rays which appear to be homogeneous by this method of investigation can often be resolved into sharply separated lines when they are passed through a slit, and allowed to fall on a photographic plate after having traversed a magnetic field (see Fig. 10, Plate I). In the *magnetic spectrum* so produced, each line corresponds to a homogeneous radiation, *i.e.* to rays of definite velocity. When we investigate the absorption of such a β-radiation in aluminium, we obtain graphs which are almost straight lines, at least in the earlier stages of absorption. Fig. 11 shows the absorption of β-rays having a velocity 0·83 times that of light (5). In order to obtain a magnitude anal-

ogous to the range of α-rays, we may produce the line AB. The distance from the origin to D then represents the range of the β-rays, *i e.* the thickness of the layer of aluminium which suffices to absorb practically all the β-rays The approximate straight line form of this graph is the result of two super-imposed processes, that of scattering and the diminution in velocity of the rays (6). (For details, see p. 41.) On replacing the

FIG 11   Absorption of Homogeneous β-Rays ($v=0$ 5 $.lc$) in Aluminium

aluminium by paper (of small scattering power), the graph assumes a somewhat concave form, whereas lead (of large scattering power) gives a convex form to the graph.

• It is interesting to note that the β-spectrum of RaE reveals the heterogeneity of the β-rays from this substance, in spite of the fact that the logarithmic absorption curve (log I against t) of RaE by the ionisation method is linear in form. Moreover, the absorption curve obtained by means of a β-ray counter (cf p 18) is no longer strictly exponential, the logarithmic curve being concave on the side of the axis of abscissae , but this fact does not, in itself, prove the hetero-

geneous nature of the β-radiation from RaE. since in the counter method a smaller proportion of the scattered β-rays is effective than in the ionisation method, and the greater ionisation of slower β-particles does not manifest itself

Fig. 12 shows the "range" of β-rays of different velocity in aluminium. Along the abscissa axis are plotted the velocities—in
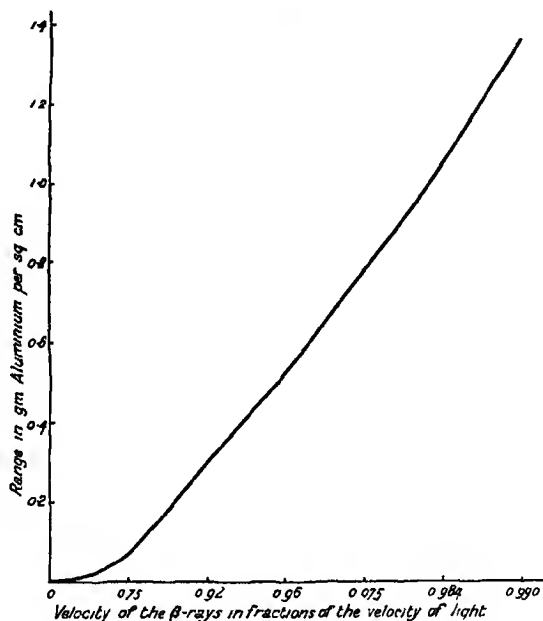
Fig 12   Range of Various β-Rays in Aluminium

fractions of the velocity of light—and the ordinates represent the range, measured in gms. of aluminium per sq. cm.* (7)   For β-rays of range from about 0·1 to 1·5 cm in air, the range as measured along the track is approximately proportional to the fourth power of the velocity, and a β-particle has a range of 1 cm. when its energy corresponds to the equivalent of about 21,000 volts (11).

The investigation of magnetic spectra (8) resulted in the detection of a large manifold of lines, of which, in the spectrum of RaC, for example, the existence of 95 has been established.   (See also p. 73.)

* In the case of aluminium with a specific gravity of 2 7, 1 gm. per sq cm. corresponds to a thickness (range) of 3 7 mm.

The fastest β-rays (0·998 of the velocity of light) were detected in the magnetic spectrum of RaC, whereas in the spectrum of ThC indications are found of the existence, along with other lines, of rays of velocity only 0 28 of the velocity of light.   In their passage through matter β-particles suffer a considerable diminution in velocity, this amounting to 30 % for rays of velocity = 0·95 that of light, after passing through 2 mm of aluminium.   In consequence of the diminution in velocity, the value of the coefficient of absorption also alters during the passage of the rays through matter.   The thickness of the half-value layer is more than ten times smaller for rays of $\frac{3}{4}$ the velocity of light than for those possessing a velocity of 95 % of the velocity of light.   The difference of the square of the energy before and after penetration of an absorbing layer is proportional to the thickness of the layer.

The decrease of velocity experienced by β- and α-rays when they pass through matter is essentially connected with the characteristic frequency of the electrons in the atoms, in a similar manner as for the phenomena of refraction and dispersion.

3 THE IONISATION PRODUCED BY β-RAYS

β-particles ionise the gas molecules lying in their track when their velocity is not less than a certain minimum value—which in air amounts to 0 0063 of the velocity of light—for in order to ionise, the particles must have a certain minimum amount of energy.   We '
can also consider with advantage the energy instead of the initial velocity of the β-particles, and since the energy of an electrically charged particle is equal to the product of charge and potential (eV), and the charge of a β-particle is always constant and equal to the elementary electronic charge, we may also introduce the drop in potential (V) in place of the energy to which it corresponds.*   In these units the above-mentioned minimum velocity corresponds to a potential of 10 volts   If we endeavour to ionise air by means of cathode rays, to which we impart the necessary energy by accelerating them in a fall of potential of sufficient magnitude, we find that a drop of 11 volts is necessary in order to obtain ionisation of

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* The physical meaning of this drop in potential is that the β-particle would have acquired the same kinetic energy if it had traversed a fall of potential of the given magnitude, and without having an initial velocity.

the air. This quantity is known as the ionisation potential of air.*
That of hydrogen has the value 17 volts, and of helium 25 volts.

In spite of their larger velocity, the ionisation produced in
a given distance by β-rays is much weaker than that effected by
α-rays. A β-particle with a velocity of about 0·9 that of light
produces in air at atmospheric pressure 55 positive and an equal
number of negative ions per cm of its path, or only about $\frac{1}{500}$ the
number produced by an α-particle. Since a β-particle collides with
8400 atoms in each cm. of its path in a gas at atmospheric pressure
and normal temperature, we are led to the conclusion that only about
1% of the atoms struck are ionised (9). Thus the large velocity of the
β-rays influences very unfavourably the yield in ions As the velocity
of the rays decreases, the total number of ions produced increases
considerably, but below a velocity of 0 028 that of light—at which
velocity 7600 ions are produced per cm —it again begins to diminish.
Corresponding to complete absorption, a β-particle produces about
10,000 pairs of ions in air ; the mean value of the number of pairs of
ions produced per 1 cm. of path is about 70 at normal pressure. The
diminution of energy of a particle reappears as work of ionisation (10).

The above data refer to the total ionisation produced by β-rays
in a gas This is in general several times greater than the primary
ionisation. by which we understand the number of atoms from which
electrons are ejected by the direct action of a primary β-particle.
By counting the droplets (ions) along β-ray tracks, it has been found
that for β-rays of velocity 10^{10} cm /sec the primary ionisation has
a value of about 90 ions per cm in air at atmospheric pressure, and
varies approximately as the inverse square of the velocity (11).

The number of ions produced per 1 cm of path in one and the
same gas is proportional to the density of the gas, so long as the gas
is attenuated ; for gases of different nature. this proportionality
between ion-number and density has only approximate validity.

4. SCATTERING OF β-RAYS

Whereas the scattering experienced by α-rays in their passage
through matter is detectable only by accurate observations, and does
not have any practical effect on absorption measurements, in the

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* The ionisation potential can also be defined as the potential with which
we have to multiply the elementary charge in order to arrive at the work
that must be performed to remove the electron from its normal orbit
within the atom to an infinite distance. (See p. 65.)

case of β-rays it is very important, and it is not permissible to neglect it. Thus the ionisation current produced in an electroscope by β-rays that have passed through an absorbing layer (e.g. aluminium foil) is considerably greater when the foil is situated in the immediate neighbourhood of the electroscope, than when it is immediately in front of the radioactive source, which is usually placed at a distance of several centimetres from the electroscope. In both cases part of the rays is scattered in traversing the aluminium foil, but whereas in the former case almost the whole of the scattered radiation reaches the electroscope, in the latter it does not (12).

The exceedingly intense scattering experienced by β-rays even when they only pass through quite thin sheets of aluminium is shown very clearly in the photographs reproduced in Fig. 13, Plate I (13).

These photographs were obtained by allowing the β-rays emitted from a few millicuries of radium emanation to pass through a small circular opening, and then to fall on a photographic film wrapped in black paper. When the experimental vessel is evacuated during the exposure, the pencil of rays is registered on the developed film as a sharply defined circular area of blackening   The introduction of a sheet of aluminium of only $0 \cdot 7 \cdot 10^{-4}$ cm. thickness in the path of the rays is sufficient to produce a distinct scattering of the rays, i e. a diminution in sharpness of the edge of the area of blackening, as seen in the figure. For aluminium foil of thickness $50 \cdot 10^{-4}$ cm. the scattering is already so appreciable that the central spot is almost invisible.   Of course the total intensity of the rays remains practically unaltered, but it is now distributed over so large an area that the blackening superimposed on that resulting from the γ-rays vanishes.

For the purpose of determining the magnitude of the scattering caused by different substances, we first measure the ionisation (I) produced in a β-ray electroscope by a β-rayer situated on a supporting plate, the thickness of which is as small as possible. The resulting ionisation is produced exclusively by particles that enter the electroscope directly. If we now place a plate of the substance under investigation immediately beneath the radioactive source, a part of the rays emitted in the downward direction, which do not under normal circumstances reach the electroscope, is now deflected from the plate in consequence of scattering, and the total resulting ionisation (I') in the electroscope is greater than I. The so-called percentage reflexion from the plate is given by $100 \cdot \dfrac{I'-I}{I}$; it

increases considerably with the atomic weight of the reflector, as can be seen from Table VIII. The data have reference to the β-rays emitted by RaE, and correspond to thick sheets of the reflectors.

TABLE VIII

Reflexion of the β-Rays from RaE from Different Substances

Substance	Atomic Weight	Percentage Reflexion
Bi	209·0	70·9
Pb	207 2	70 2
Au	197·2	67 8
Ag	107·9	57·4
Cu	63 6	44 7
S	32 1	32·1
Al	27·1	30 0
C	12 0	17·1

The number of particles reflected increases with increasing thickness of the layer (6), from which it follows that the reflexion does not take place at the surface of the reflecting substance as in the case of light rays, but in such a way that the β-rays in penetrating the atoms of the reflector are often so strongly deflected from their path that this deflection bears a resemblance to reflexion   The deviation of the β-rays is a consequence of the electrical forces existing within the atoms, and we shall return to this subject on p. 62.   The particles reflected in this manner now pass through the atoms of the reflector in the reverse direction, and so reach the electroscope.   The increase in the number of reflected particles ceases when the thickness of the reflecting layer is sufficient to completely absorb the reflected β-particles in their return journey through the layer.

We must draw a fundamental distinction between scattering through a small angle (up to about 15°), and that through a large angle (from about 60° upwards)   In the first case the scattering arises by superposition of the many small deflections suffered by the β-particle in traversing the individual atoms (" multiple or compound scattering "), whereas the scattering through large angles is caused by the β-particle approaching very closely the nucleus (cf. p. 62) of a single atom, which results in a sudden strong deviation of the particle from its rectilinear path (" single scattering ").   In single or

simple scattering, the influence of the small additional deflections due to compound scattering have quite a minor significance. (See p. 78.)

For thin layers it is found that the mean angle of deflection of a β-particle after passing through a layer of thickness x is proportional to the square root of x. For very small thicknesses the scattering is smaller than would be required by the square root law. If we compare the scattering in different elements for very small thicknesses, we find a greater scattering for elements of large atomic weight than would result if the scattering were proportional to the ordinal number. The most probable angle of scattering is inversely proportional to the energy of the rays, but this relation has not yet been firmly established for high velocities.

The scattered rays are almost always less penetrating than the original rays, because they usually suffer a diminution in velocity during the process of scattering

For the determination of the " true " coefficient of absorption we require a knowledge of the effect of scattering, and must eliminate this effect by calculation. The coefficient of absorption (or, more exactly, " coefficient of weakening ") discussed on p. 33 can in reality be resolved into a true coefficient of absorption, and a coefficient of scattering. The " atomic coefficient of absorption " (the product of the true coefficient of absorption and the atomic number, divided by the density) is found to be approximately constant within a period of Mendeléeff's classification of the elements (*14*)

5. Comparison of the Absorption and Scattering of α- and β-Rays

Whereas the velocity of all the α-particles emitted by a unitary substance (*e.g.* RaF) diminishes uniformly in their passage through matter, so that the pencil of rays remains homogeneous, and the number of them practically unchanged, the behaviour of β-rays in traversing matter is different. Here more and more particles are cut out by scattering during the transmission, and hence in the later parts of the path the ionisation is due to only a small fraction of the particles emitted by the radiating source. This decrease in the number of the β-particles is only partly counteracted by the increase in the ionising action resulting from the reduction of velocity (see p. 38), and hence the curves of ionisation (ionisation as ordinate and

velocity as abscissa) of β-rays show a downward trend from the beginning onwards, in contrast to the curves for α-rays.   Such a curve of ionisation of β-rays (and hence also a curve of absorption) is the result of various factors, of which the chief are the decreasing number of the ionising particles, the magnitude of the ionisation produced by a β-ray which at first increases as the velocity of the ray diminishes, and the additional ionising action of the scattered β-particles.   These last include both those resulting from the action of the nuclear charges, and those that have been scattered by the electron shells of the atoms traversed   When they traverse matter, homogeneous β-rays thus become appreciably heterogeneous quite near the beginning of their path, and the exponential form of the ionisation and absorption curves of these rays is only the resultant of the different contributory processes mentioned   On the other hand, if we follow out the tracks of *single* β-particles, we obtain a definite range, just as with α-rays (cf. p 35).

IV

THE γ-RAYS

1. The Nature of γ-Rays

THE third type of rays that we encounter in the investigation of radioactive processes is the γ-radiation (1) This is influenced neither by the presence of an electric nor by that of a magnetic field, and it represents a radiation similar in nature to that of light, in contrast to α- and β-rays, which consist of particles projected rectilinearly from the radioactive substance. It is closely related to Röntgen radiation and, like this, it is a form of ultraviolet light of particularly short wavelength. With the aid of interference phenomena in crystals, the spectral resolution of γ-rays has also been partially * successful, as with X-rays

. When a cylindrical pencil of Röntgen or γ-rays is incident on a crystal, diffracted Röntgen or γ-rays are emitted in different directions from the parts of the crystal involved, in a similar manner to the way in which rays of light are diffracted from a diffraction grating. We can picture the production of the diffracted Röntgen rays most clearly by regarding them as a reflection of the original rays from the lattice planes in which the atoms are situated within the crystal. If only one such crystal plane were available, all the Röntgen rays would be reflected, independently of their " colour " or wavelength There are, however, innumerable such lattice planes in the interior of a crystal, and these are separated from each other by equal distances (d). Thus the more or less penetrating Röntgen rays manage to reach many of these planes, and the radiation is reflected at all of them. But these reflected rays suffer interference and with a few exceptions annul each other. Those rays will not be annulled for which the following simple relation exists between their wavelength (λ), the glancing angle φ—i e. the angle between the incident ray and the lattice plane—and the distance (d) separating two lattice planes :

$$n\lambda = 2d \sin \varphi.$$

* The wavelength of penetrating γ-radiation is so small that even crystals are of no avail here as diffraction gratings.

In this expression n is an integer, 1, 2, 3, etc., and indicates that
reflexion also takes place for those angles the sines of which are
double, treble, etc., that of the smallest effective angle. The intensity
corresponding to these successive integers, however, becomes smaller
and smaller, just as in optics the spectra of the second, third, etc.,
orders become successively weaker. In fact, the formation of
Röntgen spectra as just described is analogous to the resolution of
light by means of a grating The so-called *lattice constant* is here the
distance between two adjacent lattice planes in the crystal; it is
of a much smaller order of magnitude than in optics, owing to the
much smaller wavelength of the Röntgen rays For instance, in
the case of a crystal of rock-salt, d amounts to only 2 80 . 10^{-8} cm.,
whereas the grating space of a Rowland grating is about 10^{-4} cm.
If we rotate the crystal when a narrow pencil of " white Röntgen-
light " is incident upon it, i e. a continuous spectrum such as is given
by an X-ray tube, we find that for each of several definite values of
the angle φ a homogeneous " Röntgen-colour " is reflected with
particular intensity, and superposed on the uniform scattered
radiation. The presence of such a Röntgen spectral line can be
recognised either by means of a photographic plate, when a sharp
line appears, or by means of an electroscope, which experiences a
sudden increase in its discharge rate for each effective setting of
the crystal

If φ and d are known, we can obtain the value of λ directly from
the formula, $i.e.$ the wavelength of the Röntgen- or γ-line in question.
For example, it is possible by the method described to establish the
existence of more than twenty separate lines in the γ-spectrum of
RaB + RaC, their wavelengths lying between 0 71 . 10^{-9} and
1·365 . 10^{-8} cm. Furthermore. by applying the method of counting
to the study of the γ-rays of high frequency from RaC, as reflected
from calcite, a still shorter wavelength of 0·27 . 10^{-9} cm. (= 27 X.U.)
has been detected. However, in the case of γ-rays of very short
wavelength, the method of crystal analysis fails, because the lattice
constant is then too large for the wavelength. But even here we are
able to reach our objective by use of another method, which involves
the calculation of the wavelength of the γ-rays from the energy of
the secondary β-rays produced by them (see p 74).

The wavelengths of the various aether waves are collected
together in Table IX.

TABLE IX

Wavelengths of the various Aether Rays

Type of Rays.	Wavelength in cm
Electric waves (2) - -	From ∞ to about 10^{-1}
Infra-red waves - -	ca 10^{-1} to 8 . 10^{-5}
Visible light - - -	8 10^{-5} to 4 10^{-5}
Ultra-violet waves -	4 . 10^{-5} to ca. 10^{-7}
Röntgen waves - -	ca 10^{-7} to 10^{-9}
γ-waves - - -	1·4 10^{-8} to ca. 5 . 10^{-11}.

The shortest Röntgen waves hitherto obtained can be produced by means of electron tubes. The principle of their action consists in the fact that, whereas in other Röntgen tubes the few remaining gas ions serve to carry the current through the tube, in an electron tube the carriers of electricity are electrons emitted by an electrically heated tungsten cathode. The highest potential with which an electron tube has been worked amounts to 308,000 volts. Under these circumstances, the hardest Röntgen rays known were produced; their wavelength was less than 10^{-9} cm., as measured spectrographically and calculated from the value (6·5 cm.$^{-1}$) of the coefficient of absorption in lead (see p. 49). The coefficient of absorption of the hardest γ-rays from RaC in lead is only 0·48 cm $^{-1}$ or about fourteen times smaller. In this region, where, as mentioned above, the spectrographic method of determination of wavelengths becomes useless, it is also no longer possible to calculate the wavelength from the absorption coefficient, but a rough estimate (3) indicates that the wavelength of the hardest γ-rays from radium has a value of about 5 . 10^{-11} cm. (see also p. 75). In order to produce Röntgen rays of this wavelength it would be necessary to have recourse to voltages of more than two million volts.

2 ABSORPTION OF γ-RAYS

The shorter the wavelength of γ-rays, the greater is their penetrating power through matter, or the greater their " hardness." If we plot the thickness of the layer traversed as abscissa, and the intensity of the radiation as ordinate, we again obtain to a first

approximation an exponential curve,* as with the β-rays. But here the coefficient of absorption μ is usually much smaller, *i.e.* the thickness of the half-value layer $\left(= \dfrac{0\cdot693}{\mu} \right)$ is much larger. Whilst the intensity of the most penetrating β-radiation falls to half its initial value after passing through 0·51 mm. of aluminium, a sheet of lead of thickness 1·4 cm. is necessary to reduce the intensity of the hardest γ-rays to one half.†

With increasing density of the absorbing substance the coefficient of absorption generally increases, but not always, as can be seen from Table X, in which are given the absorption coefficient (μ) of the most penetrating rays from RaC and μ/density for different substances (4) The substances are arranged in order of decreasing density.

TABLE X

Absorption Coefficient of the γ-Rays of RaC in Different Substances

Substance.	μ	$\dfrac{\mu}{\text{Density}}$
Hg	0 621	0 045
Pb	0 533	0 047
Cu	0 395	0 044
Fe	0·356	0 045
Sn	0 299	0 041
Zn	0 322	0 045
Al	0 126	0·047
S	0 091	0 046
Water	0 055	0 055
Air 15° C	4 64 10^{-5}	0 0378

Substances on which γ-rays impinge emit the so-called characteristic radiation of the substance, and this is added to the transmitted primary rays, as will be discussed on p 57 This phenomenon, and particularly the fact that the characteristic radiation is related in a simple manner not to the density but to the atomic number of the substance on which the rays fall, enables us to appreciate in advance that μ cannot be strictly proportional to the density of the absorbing substance.

* Here again we have $I = I_0 \; e^{-\mu x}$, where I_0 is the intensity before transmission through the thickness x, and I is the intensity after transmission.

† For instance, in order to absorb half the α-, β-, and γ-rays from the active deposit of thorium, we require 0·003, 0 2 and 15 cm. of paper respectively.

In Table XI the coefficients of absorption of the γ-rays of different radio-elements are collected together, the results having been obtained with aluminium. The softest of the rays referred to are those of ionium ($\mu = 1088$), and the hardest those of ThC'' ($\mu = 0.0916$). It will be seen from the table that a simple radio-element can emit γ-rays of different hardness, just as with the β-rays already discussed.

TABLE XI

Coefficients of Absorption of Different γ-Rays in Aluminium

Radio-element	μ	Radio-element	μ
RaB	230	Ra	354
	40		16 3
	0 57		0 27
RaC	40	MsTh$_2$	26
	0 230		0·116
	0 127		0 119
ThC'''	0 096	Io	1088
	0·0916		22·7
			0 408

For practical purposes (5) we can conveniently differentiate between very soft, soft, medium, hard and very hard rays, since the coefficients of absorption are not evenly distributed over the whole region, but fall together into definite groups. For the softest rays μ lies between 1088 and 354, the soft rays have a μ between 230 and 120, the rays of medium hardness lie between 45 and 26, the hard ones between 0 51 and 0 36, and the hardest rays between 0·198 and 0 092

Under certain circumstances, the measurement of the absorption of the γ-rays caused by layers of different thicknesses can serve for the qualitative and quantitative detection of the presence of different radio-elements, exactly as in the case of the α-rays already discussed. This method can also be used to find out whether a preparation that must not be opened consists of mesothorium or of radium, and eventually, in the former case, when the preparation was made. This result is rendered possible by the fact that the penetrating γ-radiation from radium is derived exclusively from RaC (0·50 cm.$^{-1}$ in lead), whereas in a mesothorium preparation there exist two hard γ-rayers, MsTh$_2$ (0·62 cm.$^{-1}$ in lead) and ThC'' (0·462 cm.$^{-1}$ in lead).

Now whilst $MsTh_2$ is in equilibrium with $MsTh_1$ only a few days after the preparation is made, the ThC″ radiation gradually increases during several years, corresponding to the growth of RdTh, and hence the harder ThC″ radiation in mesothorium preparations must be more strongly represented, the older the preparation is. The presence of a particularly hard radiation manifests itself by virtue of the fact that, compared with a definite γ-radiation, e g that of a radium preparation, thick plates of lead suppress the ionisation less than in the case of a softer radiation (6).

<div align="center">

TABLE XII

Radium-Equivalent of Mesothorium and Radiothorium Preparations
of Different Age

</div>

Preparation	Thickness of Lead in cms								
	0 5	1 0	2 0	3 0	4 0	5 0	6·0	7 0	8 0	9 0
MsTh - fresh	1 00	1 02	0 96	0 88	0 79	0 71	0 64	0 60	0 57	0 55
„ „ ca 3 yrs old	1 35	1·38	1·38	1 35	1 32	1 29	1 27	1·27	1 29	1·32
„ „ ca 9 yrs old	0 90	0 93	0 97	1 00	1 02	1 04	1 07	1 11	1 15	1 20
RdTh - - -	1 00	1 06	1 17	1 28	1 40	1 52	1 64	1 76	1 89	2 02

The accompanying Table XII illustrates the behaviour, as regards absorption, which is found with mesothorium preparations of various ages (7); the measurements were performed with mesothorium containing about 20 % radium * The values are expressed as multiples of the ionisation produced by a radium preparation, used as a standard. From this Table it is clear that when we have no knowledge of these conditions, the amount of mesothorium present is underestimated in the case of young preparations, and particularly by the use of thick sheets of lead As the age of the preparation increases, the amount of mesothorium is overestimated, and later, again underestimated. Moreover, if radium be present in the mesothorium, in a higher or lower concentration than is usual in technical mesothorium, this fact can be detected by the corresponding alteration of the process of absorption Nevertheless, the quantitative estimation of the different substances is fraught with great difficulty, chiefly because we almost always have to deal in practice with mixtures of mesothorium of unknown age with the element radium. Owing to

* The radium content of all mesothorium preparations derived from Brazilian monazite amounts to 20 or 25 %. (Cf. also Fig. 37 on p. 185.)

their practical importance, absorption measurements with radio-thorium have also been included in Table XII.

There exists a relation between the coefficient of absorption μ and the wavelength λ, which is quite well represented by means of the equation

$$\mu = \text{const.} \times \lambda^{2\,8}.$$

When we are dealing with homogeneous rays, the wavelength can be directly calculated (8) from the coefficient of absorption by means of this equation The value of the constant factor depends on the nature of the absorbing substance. This relation is no longer valid for those short-waved γ-rays for which the coefficient of absorption of the scattered radiation produced is of the same order of magnitude as that of the primary radiation Hence it cannot be utilised in wavelength determinations of hard γ-rays.

3. IONISATION PRODUCED BY γ-RAYS

The γ-rays do not ionise directly, but split off electrons from the molecules with which they collide, and these electrons, as β-rays, ionise the available gas molecules.

The quantity of RaC in equilibrium with 1 gm. of radium emits γ-rays, which produce a total of 11 10^{14} pairs of ions per sec in the length of their path. This number is almost equal to the number of ions produced by the β-rays from the same quantity of RaC, but since the length of the track of γ-rays far exceeds that of β-rays, it follows that the γ-rays produce in consequence many fewer ions for each cm. of their path (N B —Under normal conditions the half-value thickness of air for the γ-rays amounts to 150 m., the corresponding thickness of air for β-rays being 0·63 m.) As mentioned on pp 32 and 38, it has been established that each disintegrating RaC atom emits a β-particle, and that this produces 54 ions along one cm. of its path. In a purely formal manner we may also speak of single γ-impulses, and calculate that a γ-" particle " produces 1·5 pairs of ions per unit of length. Such a purely formal corpuscular conception of γ-rays often simplifies the solution of problems relating to γ-rays, and use is frequently made of it (9). Moreover. the number of γ-rays emitted per sec. by the amount of RaB + RaC in equilibrium with 1 gm. Ra has been found to be 7·28 . 10^{10}, which indicates that each disintegrating atom emits one γ-ray. [Cf. Ch. VII, Note (3).]

4. Scattering of γ-Rays

Since γ-rays split off β-particles from all substances, and not only from gas molecules, the action of γ-radiation on an electroscope must depend on whether the absorbing medium (e g. a lead plate) is situated near to the radiating substance or to the electroscope, for in the former case the freed electrons (so-called secondary rays) from the lead will reach the electroscope in a much lesser degree than in the latter (10). In like manner the γ-rays liberate electrons from the whole neighbourhood of the electroscope, from the walls of the room, from tables, etc , and these in their turn produce γ-rays This disturbing influence of the surroundings in the measurement of the absorption of γ-rays can be eliminated by completely enclosing the active source in a spherical shell of the absorbing substance. By using electroscopes, i e ionisation chambers, lined with paper or other light substances, we can minimise the disturbing action of the concomitant secondary rays This will be clear from the discussion in the following chapter, a knowledge of which is necessary before we can understand the phenomenon of the scattering of γ-rays in its entirety.

Generally speaking, the wavelength of the γ-rays and Röntgen rays is not influenced by the process of scattering. But in the case of very short waves it has been observed that the scattered radiation has a somewhat longer wavelength, and hence smaller energy $(h\nu = \frac{hc}{\lambda};$ see p. 79) The difference in energy between the primary and the scattered radiation is expended in liberating electrons of short range from the atoms upon which the radiation is incident (see also p 79) , these electrons can be detected photographically (see p. 78), or by ionisation methods (" Compton Effect ") (11).

V

SECONDARY RAYS

(THE INTER-PRODUCTION OF THE DIFFERENT KINDS OF RAYS)

1. THE NATURE OF THE SECONDARY RAYS

THERE exists an extended interaction between corpuscular rays (the β-rays and in a lesser degree the α-rays) and rays of an electromagnetic nature. Röntgen rays arise when the cathode rays falling on the anti-cathode of a Röntgen tube are brought to rest; in an analogous manner γ-rays are produced when β-rays lose their velocity in their passage through matter. In their turn Röntgen- and γ-rays knock off electrons or so-called secondary β-rays from the atoms on which they impinge, and provided they have sufficient energy, these will again liberate secondary γ-rays, and so on.

• β- and γ-rays that have originated in this secondary manner are briefly designated *secondary rays*, whereby we embrace the rays of secondary origin produced by α-rays. Scattered primary rays, which are with difficulty or not at all distinguishable from the secondary rays. are also often included among the secondary rays.

The most important properties of the secondary rays are discussed in what follows.

2. SECONDARY β-RAYS PRODUCED BY γ-RAYS

The *initial velocity* of the β-rays excited in matter by γ-rays is independent of the intensity of the γ-rays, and to a first approximation independent of the nature of the material (1), *e.g.* the β-radiation produced by the γ-rays of RaC is found to be independent of the material in which it is excited, and possesses an absorption coefficient in aluminium of about 20, to which corresponds a half-value thickness of 0·35 mm. On the other hand, the initial velocity is dependent on the hardness of the exciting γ-radiation; the shorter the wavelength of this, the higher the velocity of the resulting β-particle.*

* The following relation exists between the maximum energy of the secondary β-rays produced (eV) and the frequency of the γ-rays (ν) producing them ·
$$U = eV = h\nu. \quad \text{(Cf. p. 53.)}$$

The *number* of the secondary β-particles is proportional to the intensity of the absorbed γ-radiation, and increases with the atomic weight of the material used.

The secondary rays are emitted in various directions, but the direction coinciding with that of the primary rays predominates, especially in the case of materials of small atomic weight. According as to whether the secondary rays are emitted from the side of the sheet on which the primary rays are incident or from which they emerge, we speak of "incidence" or "emergence" radiation.

The intensity of the incidence radiation increases asymptotically with the thickness of the material, and reaches half of its maximum value in the case of aluminium for a thickness of 0 5 mm ; it also increases with the atomic weight of the secondary radiator, as shown by the numbers in Table XIII.

TABLE XIII

Dependence of the Incidence Radiation on the Atomic Weight

Substance	Intensity of the Incidence Radiation in Relative Units
Lead - - -	7
Copper - - -	4
Iron - - -	3 7
Aluminium - -	2 1
Paper - - -	1

It is also immediately clear from the above numbers that, as already mentioned on p 50, we can greatly minimise the influence of the secondary rays generated in the walls of the electroscope during the measurement of γ-rays, by making use of an electroscope constructed from paper, or lined with it. But special precautionary measures are still necessary in order to reduce the secondary β- and γ-radiation from the walls of the room, and from tables, etc.

For all materials hitherto investigated, with the exception of lead, the intensity of the emergence radiation exceeds that of the incidence radiation. As contrasted with the latter, the emergence radiation increases with increasing thickness of the material until it reaches a maximum value, after which it diminishes.

3. ELECTROMAGNETIC RAYS PRODUCED BY ELECTRONS *

In order to produce Röntgen rays of wavelength λ, cathode rays must possess an amount of energy and a corresponding velocity that is greater, the less the value of λ, *i.e.* the greater the " hardness " of the γ-rays produced The greater the available energy of the cathode rays is, the more considerable will be the hardness of the γ-rays. The following relation holds when, instead of λ, we consider the frequency (ν) of the γ-radiation, given by the quotient of the velocity of light and the wavelength .

$$U = eV = h\nu ,$$

where U is the energy of the cathode rays, V is the discharge potential (see p. 45), and the constant h is the " elementary quantum of action." † From this relation it follows that the shortest wavelength that can be excited by the aid of a discharge potential of 2500 volts is of magnitude $4\cdot88 . 10^{-8}$ cm., and that, for instance, in order to excite Röntgen radiation of a hardness equal to that of the softest γ-radiation from RaB ($\lambda = 1\cdot365 . 10^{-9}$ cm) we should require a minimum potential on the discharge tube of 89,000 volts. Since the wavelength of the hardest γ-radiation from RaC is not known with certainty, it is not possible to calculate exactly the potential that would be necessary to produce a correspondingly penetrating radiation in a Röntgen tube, but an estimate yields the value of about 2 million volts

Whereas the validity of the above discussion is independent of the chemical nature of the radiating source, we shall discuss in what follows the influence of the nature of the source on the character of the Rontgen radiation emitted.

If, for instance, cathode rays impinge on a rhodium anti-cathode in a Röntgen tube, an investigation of the Röntgen radiation emitted by it shows the presence, together with a heterogeneous " white " radiation, of several sharply defined types of rays, from amongst which the shortest has a wavelength of $0\cdot534 . 10^{-8}$ cm. This radiation is as *characteristic* of rhodium as the D-lines in optics are

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* It has been possible to investigate the excitation of Rontgen rays by cathode rays on a much broader basis than the excitation of γ-rays by β-particles.   In view of the close analogy of the two cases and the importance of this class of phenomenon, the behaviour of Röntgen rays is also treated here

† Planck's constant, $h = 6\,54 . 10^{-27}$ erg. sec.   Further details will be found in advanced text-books on physics.

characteristic of sodium.*　　As required by the above formula, it ceases to occur as soon as the discharge potential sinks below about 23,000 volts.　Further lines of the rhodium spectrum, those of the L-group, can only be detected by the use of a vacuum spectrograph, for they are so soft that a layer of air of 20 cm thickness almost completely absorbs them　　Fig 14 (Plate I) shows the L-emission spectrum of hafnium, which was obtained by having a small quantity of a salt of hafnium on the tungsten anti-cathode of a Rontgen tube. In addition to the hafnium lines, a few of the L-lines of tungsten appear on the photograph, as well as the lines K_{a_1} and K_{a_2} of copper, which was also present on the anti-cathode　　These copper lines serve as useful reference lines.　Furthermore, Röntgen spectroscopy enables us to detect with ease and rapidity the presence of similar quite small traces of impurity in the material of the anti-cathode, provided they do not amount to less than 0 1 to 0·01 %.

As already mentioned, both Röntgen- and γ-rays arise when quickly moving electrons strike solid bodies, and thereby lose their velocity within a very short distance.　If for purposes of comparison we take an illustration from acoustics, we may liken the state of vibration of the rays occurring in a Röntgen tube more to a sharp report than to a musical tone　　Along with this impulse radiation resembling a detonation, a second kind of Röntgen radiation arises when an electron strikes matter　It proceeds from the atoms of the body struck, and is the characteristic radiation of the type of atom involved, or, returning to our acoustical analogy, it corresponds to the tone arising from resonance of the relevant body　　In respect of the distribution of wavelengths over the spectrum, the difference between the two types of radiation is most clearly brought out by having recourse to an optical analogy　The impulse radiation corresponds to continuous white light, whereas the characteristic radiation has its optical analogue in a line spectrum.

In the Röntgen spectrum we differentiate between the K-, L-, M-, N-, O- and P-series,† the wavelengths of which increase as we

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* Just like the D-line, the strongest rhodium line also consists of a doublet ($0·614 . 10^{-8}$ and $0·619 . 10^{-8}$ cm.).

† The M-series has only been observed for elements of higher ordinal number that 65, and the N-series only in the case of the elements Bi, Th and U.　It has been found necessary to differentiate between several " levels " in certain series.　Thus for the heaviest of the elements we have 1 K-, 3 L-, 5 M-, 7 N-, 5 O-, and 3 P-levels (see also p. 68).

pass from series to series. Fig. 15 shows a schematic representation of the relative positions of the first three series. As far as we know at present, 12 lines at most belong to the K-series, and 22 to the L-series. These lines can be divided into different sub-groups. Whereas in the K-series we distinguish only one such group, we find three in the L-series and five in the M-series. The excitation potential of the cathode rays producing them is the same for all lines of the same group. The characteristic rays of an element are simply related to its ordinal or atomic number. Thus for the frequency (ν) of the strongest line of the K-series the following approximate relation holds : *

$$\sqrt{\nu} = \sqrt{\tfrac{3}{4}} \cdot \nu_0 \cdot (N-1),$$
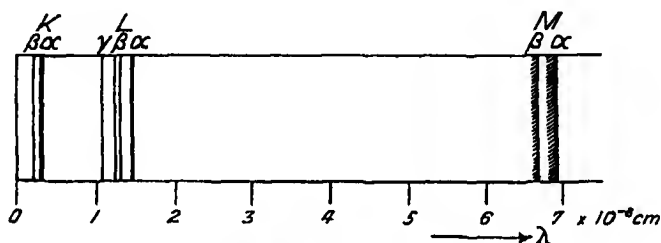
FIG 15   Wavelengths in the K-, L-, and M- series

where $N =$ atomic number (for $H=1$, $He=2$, $Li=3$, etc), and $\nu_0 = 1 \cdot 09737 \cdot 10^5$ cm $^{-1}$, or the so-called Rydberg constant, well known in optics

Apart from only a small systematic deviation (cf p 67), the following formula holds for every line of the characteristic spectrum :

$$\nu = A(N-B),$$

where A and B are constants, and N is the atomic number. Thus, if we construct a graph with the atomic numbers of the elements as abscissae and the square roots of ν as ordinates, we obtain almost a straight line, as seen in Fig. 16, the data of which refer to the strongest line of the K-, L- and M-series respectively We shall speak later of important conclusions which may be drawn from this regularity. Suffice it to say at this juncture, that therein alone is manifested the

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* The frequency here referred to is in reality the " wave number " $(1/\lambda)$, or number of waves per cm., as compared with the true frequency $(=c/\lambda)$ already mentioned.
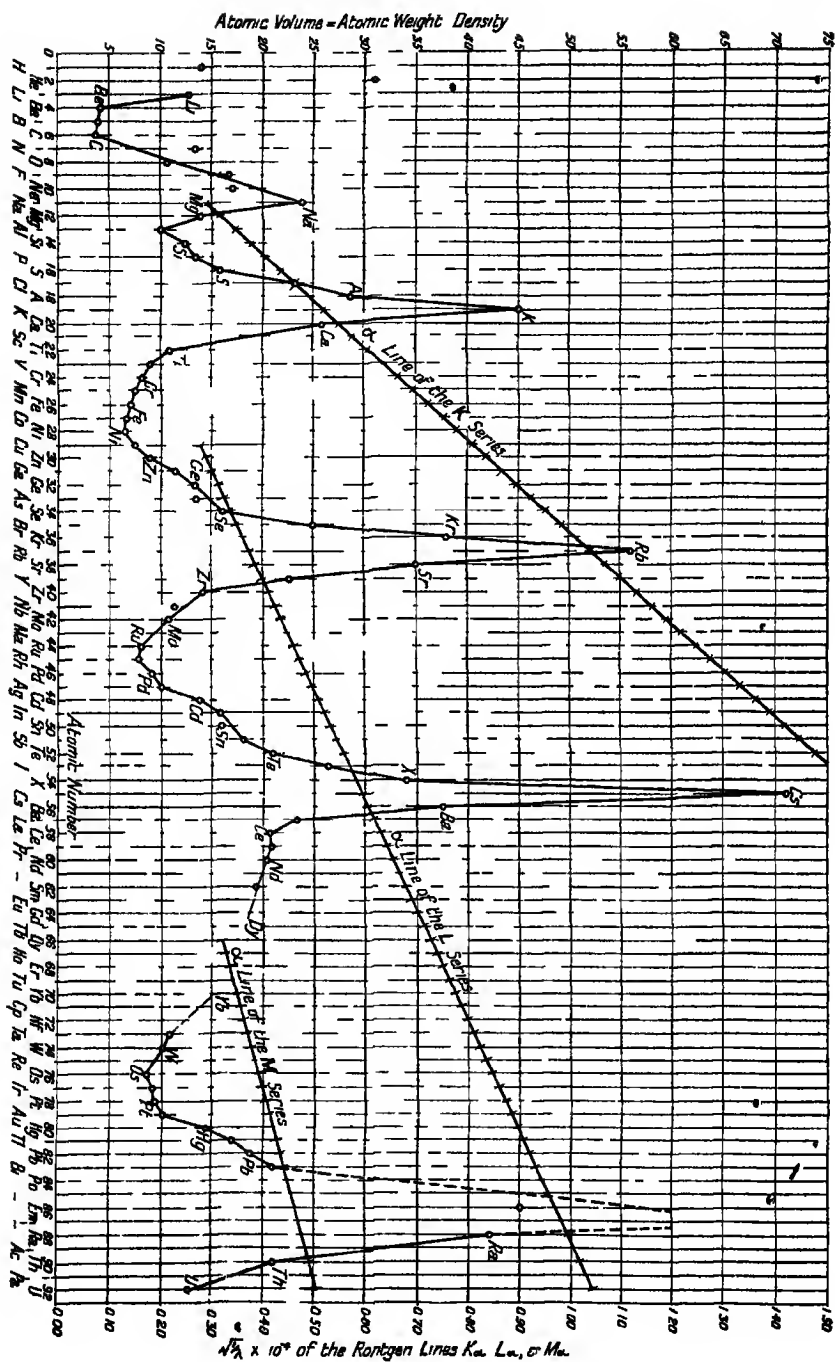
FIG 16   Atomic Volumes and Röntgen Spectra of the Elements

superiority of the atomic number over the atomic weight for the principle of the classification of the chemical elements, for if we choose the atomic weight as abscissa, we do not obtain straight lines, but irregular ones.

The production of characteristic rays results also from the action of Röntgen rays, when their frequency slightly exceeds or at least equals that of the characteristic limiting frequency (see p. 53). It is the same condition as that with which we meet in optics in connection with the occurrence of fluorescence according to Stokes' law. A fluorescence radiation can be called forth only by a radiation that lies further towards the violet end of the spectrum. Since most γ-rays are of high frequency, they are able to excite the characteristic radiations of many substances in their passage through them, and this gives rise to a considerable complication of the phenomenon of absorption, apart from the complications arising from the scattering of the γ-rays and the appearance of secondary rays. We have already mentioned on p. 46 that no simple relation exists between the coefficient of absorption of the γ-rays and the density of the absorbing medium.

4. Secondary Rays Produced by α-Rays   δ-Rays

Secondary β- and γ-rays may also arise when α-rays impinge on matter.

The β-particles produced in this manner have for the most part a very small initial velocity, and a correspondingly small ability to ionise, but a fraction of these particles acquires a kinetic energy corresponding to an electron that has fallen freely through a potential drop of 40 volts, or about four times the energy necessary to ionise a molecule of air (see p. 37). The so-called " δ-rays "—slow electrons emitted by all α-rayers—are also secondary β-rays produced by the α-particles. Thus when an α-particle strikes an atom, its kinetic energy is partially dissipated, and a fraction of the electrons taking part in this process acquire a velocity sufficient to carry them beyond the confines of the atom. The energy of the δ-rays can be calculated to be from 2·5 to 4·1 volts (2).

The production of δ-rays by α-rays can also be detected photographically. When the rectilinear track of an α-particle is rendered visible by the condensation of water vapour upon it (see p. 78), quite small lateral branches can be detected along the track, and they are

due to these " fast " δ-rays (3). Much of the ionisation caused by an α-particle is due to the δ-particles it liberates from the gas. That the ionisation produced by α-particles is less considerable in diatomic than in monatomic gases is due to the fact that the δ-particles are much less efficient ionising agents in the former than in the latter case (4).

This production of secondary β-rays appears to be connected with the presence of a gas layer (5) For example, with zinc that has been freed from gas by distillation in a high vacuum this effect is absent. It returns, however, when air is again admitted to the surface of the zinc.

If α-particles strike atoms of hydrogen, these are ionised and acquire very large velocities as a result of the collision, since their mass is only one quarter of that of α-particles. The range of these particles is also several times that of the α-particles producing them. In this way " H-rays " are produced in hydrogen by the α-rays from RaC, the range of these H-rays being about 28 cm

By means of scintillation observations (see p. 19) it has been possible to detect a small number of particles with a considerably greater range, when various substances are bombarded by α-rays. The observation of such H-rays, which originate in the atomic nuclei struck, was of great importance in the elucidation of atomic structure (see p 147)

When the α-particles from radium emanation are incident on lead, tin, etc , a small fraction of them succeeds in producing hard γ-rays * (μ in lead $= 1\ 8$ cm $^{-1}$) Moreover, a correspondingly small amount of the characteristic radiation of the atoms struck is excited With lead, gold, and platinum, the occurrence of the " K "- and the " L "-radiation has been observed, whilst with tin only the latter of these has been detected (6).

* The analogous production of Rontgen rays by means of canal or positive rays has also been proved

VI

RECOIL RAYS

WHEN an a-particle is emitted from an atom, the latter recoils in the opposite direction in accordance with the principle of action and reaction, just as a gun recoils when a shot is fired from it (7).

If the mass and velocity of the projectile are m_1 and v_1, and those of the gun m_2 and v_2, we have

$$v_2 = v_1 \cdot \frac{m_1}{m_2}.$$

Thus an atom of RaA emits a-particles with a velocity of 1 69 . 10^9 cm./sec., and becomes transformed into an atom of RaB, which is projected by virtue of recoil with a velocity of

$$1\ 69\quad 10^9 \cdot \frac{4}{214} = 3\ 31 \cdot 10^7 \text{ cm 'sec.,}$$

the atomic weight of the a-particle being $= 4$, and that of the RaB atom being 214. The velocity of the residual atom of RaB is considerably less than that of the a-particle, but it is sufficient to ionise the air along its track, to act on a photographic plate, etc As with the a-particles its ability to do these things ceases suddenly, the range (8) amounting to 0·14 mm. in air, and 2 . 10^{-5} mm. in silver. In consequence of their smaller velocity, the phenomenon of scattering occurs in a much more marked degree with recoil rays than with a-particles (9). From the magnitude of the deflection in a magnetic field it follows that the recoil atom has an atomic weight of about 214, which agrees well with that of RaB, and that it carries a *single* elementary electric charge (10).

If we have a deposit of, say, RaA on a horizontal metallic plate, then the atoms which emit a-particles in an upward direction will be projected downwards and will penetrate the uppermost layers of the plate (11). On the other hand, those atoms which have emitted a-particles in the downward direction will be projected upwards into the air surrounding the plate. Thus the most favourable yield of recoil atoms that have been caused to leave the plate by recoil and are then collected will be 50 % (12).

The possibility of obtaining individual radio-elements in a pure state by utilising the phenomenon of radioactive recoil plays a very important rôle in the study of radioactivity (p. 170). In order to be independent of the small range of the recoil atoms, they are collected in an electric field, i e. we charge the preparation to a positive potential of, say, 100 volts, and connect the negative pole of the battery to an insulated plate fixed above the preparation. The residual atoms are drawn through the air to the upper plate, since they are positively charged, except for a very small fraction of them (see Fig 17). After emitting the positively charged
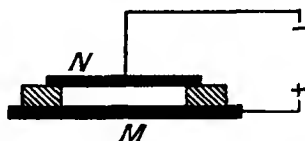
Fig 17   Arrangement for Collecting Recoil Atoms

α-particles, these recoil atoms are at first negatively charged, but when they ionise the molecules of the surrounding air in their track they part with several electrons and thus themselves acquire, a positive charge. An investigation of the deflection of the recoil atoms of RaB in a magnetic field showed that practically all of them carry a single positive charge, and only about $\frac{1}{1000}$ % of them are negatively charged (13)

The phenomenon of recoil must also occur during the emission of a β-particle, but the resulting residual atoms are much more difficult to detect than the products of α-recoil (14). The kinetic energy of the projected particle is here much smaller, and is usually insufficient to propel the particle away from the surface of the plate on which the disintegration took place. By using special precautions, such as working in a high vacuum, depositing the active material on a polished surface, etc , it has been possible to collect up to 20 % of the RaC atoms recoiled during the disintegration of RaB. Such quantitative results, however, are always liable to be complicated by the phenomenon of aggregate recoil discussed below.   •

The photographic detection of recoil atoms is only possible when the gelatine layer of the plates is so thin that the recoil atoms are ✓ not brought to rest before they reach the AgBr (15).   •

We meet with a special type of recoil in the phenomenon of so-called " aggregate recoil " (16). If we deposit polonium electro-lytically on a bright metal foil, and place a second foil near to and

facing it, it is possible to detect polonium also on the second foil after a short time. In explanation of this result, it is assumed that the polonium is not deposited on the foil in the form of individual atoms during electrolysis, but that aggregates of two and more atoms are deposited. When one of the atoms of such an aggregate disintegrates, not only does the RaG atom resulting from the disintegrated Po atom suffer recoil, but also the unchanged Po atoms present in the same aggregate are projected *en masse*. Thus when the a-particle is emitted in the direction of the first foil, the remaining aggregate, consisting of a RaG atom and one or more Po atoms, is projected in the direction of the second plate. This phenomenon supplies an explanation of the fact that all objects in the neighbourhood of strong polonium preparations become contaminated with polonium, even though this element gives off no emanation and its succeeding product of disintegration is no longer active. Aggregate recoil phenomena can also be observed with preparations in which the polonium was not deposited electrolytically, but obtained by collecting the active deposit from radium emanation. Other radio-elements that emit a-rays are found to show the same phenomenon, even the products of short life (*e.g.* RaA, RaC) that are obtained by exposing a negatively charged wire in emanation. Many anomalous results that have been obtained in experiments on such active deposits can be readily interpreted in terms of the presence of aggregates, and the degradation of these as the active material decays.

In all the cases so far discussed, we have been dealing with the recoil of material particles. Recently, however, the phenomenon of the recoil of electrons has also been established. It occurs when a single electron scatters a quantum of Röntgen rays, and is sometimes recorded on the photographs of condensation tracks of the rays .

VII

CONSTITUTION OF THE ATOM AND RADIOACTIVE RAYS

THE behaviour of the rays in their passage through matter was our most reliable guide in the investigation of the constitution of atoms, and conversely, the theory of atomic structure clears up many points on the origin and the nature of the individual types of rays. For this reason we shall now give a short account of the constitution of the atom in the light of modern research

1. THE CONSTITUTION OF THE ATOM

The model of the atom described below has gained general recognition   According to it, the material part of the atom does not embrace the whole volume of the atom, regarded as a sphere of radius 10^{-8} cm , but is limited to an exceedingly small space at the centre of the atom of about 10^{-13} cm * diameter   Moreover, this "atomic nucleus" is positively charged   The remainder, i e. practically the whole of the space inside the atomic sphere, is thus at the disposal of the electrons which revolve round the nucleus. The dimensions of this electron cloud determine the magnitude of the atom   The number of the electrons is equal to the number of units of positive electricity associated with the nucleus.   Thus the atom as a whole appears electrically neutral.

The total number of electrons revolving in the atom, and hence also the number of positive nuclear charges, is equal to the atomic number (see p 116) of the element concerned   The number of orbital electrons is thus 1 in the hydrogen atom, 2 for helium, 3 for

* This value is derived from the magnitude of the deviation suffered by α-particles when they penetrate into the vicinity of the nucleus (see p. 77). Whereas the radius of the sun is only about 400 times smaller than that of the earth's orbit, the nucleus of an atom, which resembles in its structure a planetary system, is about 10,000 times smaller than the distance of the electrons from the mid-point of the system.

lithium, 29 for copper, 78 for platinum, and 92 in the case of uranium, which is the element of highest atomic number.

When the electrically neutral atom becomes ionised, it assumes either a positive or a negative charge   In the former case, the outer electron layer loses a definite number of electrons, and in the second case the atom takes up one or more electrons from the surrounding matter or from the free electrons in the surrounding space.   Ionisation or chemical change of any kind, however, cannot produce any alteration in the number of charges on the nucleus ; hence these processes are always reversible   The reversibility of all changes produced by chemical processes in the character of the atom signifies nothing else than the long known law of the Conservation of the Elements.   On the other hand, in the relatively rare cases of radioactive processes, the nucleus, and hence also the system of electrons surrounding it, undergoes permanent transformation.   As described on p. 114, this transformation results in a complete alteration of the chemical nature of the atom, and is very intimately connected with the emission of the radioactive rays

The stability of an atom built up in the manner indicated cannot be explained on the basis of classical mechanics and electrodynamics. In order to understand it, it was necessary to formulate the hypothesis that there are certain privileged states of motion of the atom, and that the latter persists in these states without the emission of energy.   The energy content of the atom can only change when the atom passes over from one such privileged state into another.

For the interpretation of radiation processes it was necessary to introduce yet another hypothesis, according to which, when such a transition is associated with the emission of radiation, the latter is always monochromatic   Moreover, the frequency of the light so emitted is equal to the amount of energy radiated, divided by Planck's constant, h

The experimental evidence in support of the view outlined above is so diverse that it cannot be traced exhaustively here.   We shall only mention the following especially important phenomena . the scattering of a-rays in their passage through matter (p. 28), isotopy (p. 125), and the emission and absorption of light, Rontgen rays, etc , as they are revealed in the spectra of the elements.

Before we proceed to the question of the origin of the radioactive rays, it will be advisable to discuss in somewhat greater detail the structure of the atom in the simplest cases.

2. Structure of the Hydrogen Atom

A hydrogen atom consists of a nucleus, which in this case carries only a single positive charge, and an electron, which always moves in certain permissible orbits corresponding to the first hypothesis above mentioned   This motion is subject to Kepler's laws, just like that of a planet about the sun, which is situated at the focus of the orbit, and hence the privileged orbits of the electron are ellipses

There is quite a number of such stationary orbits, but one of them is unique in that when the electron is moving in it, the atom possesses a minimum content of energy   In this so-called " normal state " the hydrogen atom can persist permanently, whereas the " life " of all other stationary states is very short

In accordance with the second hypothesis already mentioned, a monochromatic pulse of waves is emitted when an electron passes over from one stationary state to another.   In Fig 18 we see the

$\mu\mu$
121 ——————— 2 —→ 1   *Transition from the second to first orbit*

102 —————— 3 —→ 1   *Transition from the third to first orbit*

94 7 —————— 4 —→ 1
92 6 —————— 5 —→ 1
———————— 6 —→ 1
———————— 7 —→ 1
91 1 —————— ∞ —→ 1   *Transition from infinity (= the ionized state) to the first orbit*

Fig 18   Spectrum of Hydrogen in the Ultraviolet Region (Lyman Series)

spectroscopic consequences of the return of an electron to its normal orbit from another stationary orbit, into which it had passed by virtue of some outside influence such as the bombardment by cathode rays. When the return to the normal orbit takes place from orbit 2, a spectral line of wavelength 121 $\mu\mu$ is emitted, whereas when the transition takes place from orbit 3, a line of shorter wavelength (102 $\mu\mu$) is

produced, because of the greater energy difference between the two orbits, and so on.   Should the return take place from an infinitely distant orbit, a spectral line of wavelength $91\mu\mu$ is emitted.   This last case is equivalent to the " neutralisation " of a hydrogen ion, since of course the converse process of the removal of an electron to infinity constitutes the phenomenon of " ionisation."   This neutralisation of the hydrogen ion thus appears, in the light of the theory of series spectra, as a limiting case of discontinuous quantum states.   The above-mentioned lines (Fig. 18) all lie in the extreme ultraviolet   The lines of the visible spectrum of hydrogen have their origin in transitions from one transitory orbit to another transitory orbit, $e\,g$. from orbit 3 to orbit 2, etc. ;   their mode of production is to be seen from Fig. 19.

Red $\mu\mu$

656 ———————— $3 \rightarrow 2$ Transition from the third to second orbit

486 ———————— $4 \rightarrow 2$ Transition from the fourth to second orbit

434 ———————— $5 \rightarrow 2$

Violet 410 ———————— $6 \rightarrow 2$
———————— $7 \rightarrow 2$

364 ———————— $\infty \rightarrow 2$ Transition from infinity to second orbit
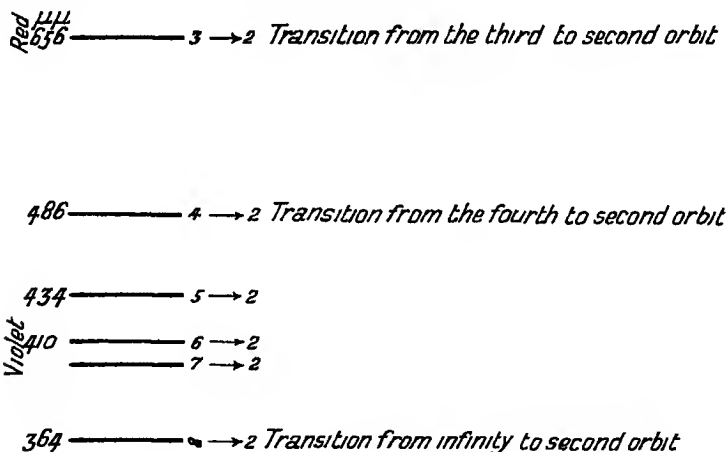
Fig 19   Spectrum of Hydrogen in the Visible Region (Balmer Series)

The relative distances of the individual stationary orbits from the centre of the atom are represented in Fig 20.   The diameter of the first orbit is that of the atom in its normal state, and is equal to $1\,06 \cdot 10^{-8}$ cm.   The calculation of the orbital radii involves only three universal constants : the elementary electrical charge e, the mass of the electron m, and Planck's quantum of action h (p. 53).   The same quantities also suffice to calculate the work that is necessary to transfer the electron from one stationary orbit to another.   For instance, we can calculate the work necessary to entirely remove the electron from the atom, and when the result is expressed in volts (see p. 37), we find the value to be 13·5 ; this is the ionisation potential of the hydrogen atom.

H P R.   E

For purposes of simplicity, the electron orbits of the hydrogen atom represented in Fig. 20 have been assumed to be circular in shape.   More detailed investigations have shown, however, that apart from stationary circular orbits, the motion of the electron may also take place in stationary elliptical orbits.   It then no longer suffices to characterise the stationary orbit by one number, but we must have recourse to a second number, in order to differentiate between the various magnitudes of the eccentricities of the orbits   These numbers are known as the quantum numbers of the orbits   As may be seen from Fig 21, the major axes of the ellipses have the same length for orbits which possess the same

Fig 20   Stationary Circular Orbits in the Hydrogen Atom
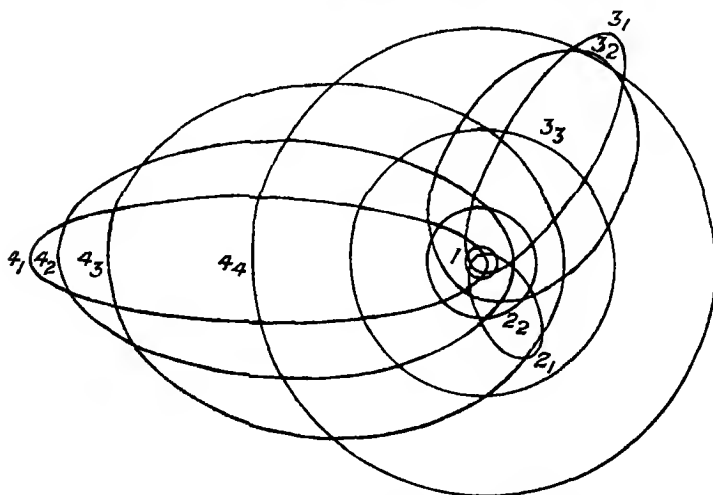
Fig 21   Stationary Elliptical Orbits in the Hydrogen Atom

first quantum number.   The minor axis varies with the second quantum number in such a manner that the orbit has its greatest eccentricity

when the second quantum number is unity, and it is circular when the first and second quantum numbers have the same value.

The regularities revealed in the spectrum of hydrogen yield unmistakable evidence of the existence of only one electron in the atom of hydrogen, *i.e.* the hydrogen nucleus must carry only one positive elementary charge. We may draw the same conclusion from the magnitude of the absorption of a-rays in hydrogen, and also from the fact that in a positive ray tube we never meet with hydrogen rays bearing a charge greater than one positive elementary unit.

3. Atoms of Higher Atomic Number

We saw on p. 55 (cf also Fig. 16) that a linear relationship exists between the square root of the frequency of a Röntgen line and the atomic number of the element involved, and hence that the Röntgen spectrum is determined, to a first approximation, solely by the nuclear charge number of the atom. It thus stands in sharp contrast to the periodicity shown by most of the other properties of the elements. Nevertheless, a more detailed investigation of the Röntgen spectra of the elements leads to the result that even here we find a dependence on other factors than the nuclear charge, *e.g.* the detailed building up of the atom. In Fig. 22 the atomic numbers of the elements are plotted as abscissae, and the square roots of the energy levels (cf. p. 46) as ordinates. We see that the ordinates reveal marked bends in the positions corresponding to the beginning and end of the rare earth group. These bends are most clearly defined in the N- and O-levels of the atom. The iron, palladium, and platinum groups show similar features. The curves of Fig. 22 can hardly be otherwise interpreted than by assuming that the electrons in the atoms are arranged in groups, and that the bends occur at places where new groups begin to form. Moreover, the study of optical spectra, and of the magnetic properties of the atoms, leads to the same result, which is also in excellent agreement with the quantum theory of atomic structure. In this theory we are faced with the following problem. We have an atomic nucleus with a definite number of positive charges, we introduce into the field of this nucleus successive electrons and enquire as to how the individual electrons will be captured and bound by the field of force. The answer is indicated in Table XIV. From this Table we can see how many electrons move in the different groups, which are denoted by their respective quantum numbers.

From amongst the atoms of higher atomic number, let us first consider the element helium. The spectral behaviour of this element leads to the assumption that in the normal state of the atom both electrons move in one-quantum orbits, $i\ e.$ in circular orbits, and that the planes of these orbits are inclined to each other at an angle of 120°. This configuration is particularly stable, in agreement with the chemical inertness of helium The exceedingly great chemical

FIG 22 Rontgen Ray Energy Levels as a Function of the Atomic Number

inertness of the helium atom also finds expression in its abnormally high ionisation- and excitation-potentials In order to remove completely one electron from the helium atom, the bombarding electrons must have traversed a drop in potential of 25 volts ;

moreover, we require a potential of 54 volts to separate the second electron from the helium atom.

As a result of recent investigations with very pure helium, the possibility of the existence of an anomalous state has been discovered, and in this state the atom can persist permanently, in contrast to the short-lived transitory states of electrons not in their normal orbit. Helium atoms can be converted into this " excited " state by bombardment with electrons of 20 volts " velocity." A reversion from this metastable state into the normal state can be brought about by chemical influences, such as the presence of traces of hydrogen and the like   From the point of view of the theory of the atom referred to above, this metastable state is identical with one of the stationary states, the existence of which is shown by the spectrum of helium   Here both electrons move in the same plane— the inner one in a one-quantum orbit, and the outer in a two-quantum orbit, or more precisely, in a 2_1-orbit (cf the analogous 2_1-orbit of the hydrogen atom in Fig. 21).

We have seen that the single electron of the normal hydrogen atom occupies a 1_1-orbit   In an atom of higher atomic number, e g. of nuclear charge 50, the first electron will also revolve in a 1_1-orbit, but in consequence of the greater attraction of the nucleus, the radius of this circular orbit will amount to only $\frac{1}{50}$ of the radius of the 1_1-orbit in the hydrogen atom.   This explains why it is that the dimensions of atoms containing a large number of electrons are of only the same order of magnitude as the hydrogen atom, which contains only one electron   As may be seen from the numbers in Table XIV, two electrons of the element neon move in 1_1-orbits, and four electrons in each of the orbits 2_1 and 2_2 Like that of the other rare gases, this configuration is of especially symmetrical construction   The eleventh electron of the Na-atom, however, is unable to find a place in the structure of neon, and it thus takes up a 3_1-orbit, from which it can be removed with relative simplicity   In this we have an explanation of the great reactivity of metallic sodium, and of the rest of the alkali metals   On the other hand, the sodium ion, which has already parted with this 3_1-electron, possesses a stability resembling that of an atom of a rare gas.

• When an additional electron finds its place in an outer group of electrons in an atom, it is clear from what has been said that the newly-formed atom must differ considerably in its chemical properties from the atom immediately preceding it.   This is the case in most

TABLE XIV

Types of Electron Orbits of the Elements

Orbit n_k	K 1_1	L 2_1	L 2_2	M 3_1	M 3_2	M 3_3	N 4_1	N 4_2	N 4_3	N 4_4	O 5_1	O 5_2	O 5_3	O 5_4	O 5_5	P 6_1	P 6_2	P 6_3	P 6_4	P 6_5	P 6_6	7_1	7_2
1 H	1																						
2 He	2																						
3 Li	2	1																					
4 Be	2	2																					
5 B	2	2	1																				
10 Ne	2	8																					
11 Na	2	8		1																			
12 Mg	2	8		2																			
13 Al	2	8		2	1																		
18 A	2	8		8																			
19 K	2	8		8			1																
20 Ca	2	8		8			2																
21 Sc	2	8		8		1	(2)																
22 Ti	2	8		8		2	(2)																
29 Cu	2	8		18			1																
30 Zn	2	8		18			2																
31 Ga	2	8		18			2	1															
36 Kr	2	8		18			8																
37 Rb	2	8		18			8				1												
38 Sr	2	8		18			8				2												
39 Y	2	8		18			8		1		(2)												
40 Zr	2	8		18			8		2		(2)												
47 Ag	2	8		18			18				1												
48 Cd	2	8		18			18				2												
49 In	2	8		18			18				2												
54 X	2	8		18			18				8												
55 Cs	2	8		18			18				8					1							
56 Ba	2	8		18			18				8					2							
57 La	2	8		18			18				8		1			(2)							
58 Ce	2	8		18			18			1	8		1			(2)							
59 Pr	2	8		18			18			2	8		1			(2)							
71 Cp	2	8		18			32				8		1			(2)							
72 Hf	2	8		18			32				8		2			(2)							
79 Au	2	8		18			32				18					1							
80 Hg	2	8		18			32				18					2							
81 Tl	2	8		18			32				18					2	1						
86 Rd	2	8		18			32				18					8							
87 —	2	8		18			32				18					8						1	
88 Ra	2	8		18			32				18					8						2 "	
89 Ac	2	8		18			32				18					8		1				(2)	
90 Th	2	8		18			32				18					8		2				(2)	
118 ?	2	8		18			32				32					18						8	

of the places in the periodic classification of the elements. In certain cases, however, the added electron becomes associated with one of the inner orbits of the atom, and the chemical nature of the element then suffers only a slight modification. We meet with an instance of this in the iron group of the elements, and in the rare-earth group the process is still more marked, for here the successive addition of electrons takes place in the somewhat deeply lying 4_4-orbits, beginning with cerium, and ending with cassiopeium. For the next element hafnium, on the contrary, the 72nd electron is bound in one of the outlying five-quantum orbits, and in consequence of this it possesses properties distinctly different from those of the rare earths

The alteration of the properties of the elements with increasing atomic number, as revealed in the periodic classification of the elements, is a direct consequence of the gradual building up of these successive electron groups. The appearance of a rare gas at certain points in the classification is evidence of the fact that at these points the distribution of electrons has reached a particularly high degree of completeness, and the corresponding elements are very stable.

Fig 23 shows the orbits of the 11 electrons in the atom of sodium. The first 10 electrons always move in the neighbourhood of the nucleus, whereas the 11th electron is situated in an elongated orbit, and only periodically penetrates into the inner part of the atom, when it approaches the nucleus of the atom very closely, however During the major part of its orbit the
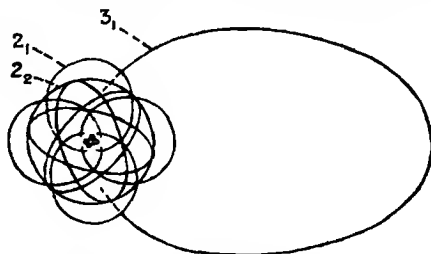
Fig 23　Model of a Sodium Atom

11th electron experiences almost the same attraction as would be exerted by a single positive charge, for the 11-fold charged nucleus and the 10 electrons act approximately as would a hydrogen nucleus Periodically, however, when the 11th electron comes into the immediate proximity of the nucleus, it is subject to the total attraction of the 11 positive charges. This attraction will give rise to a very marked increase in the velocity of the 11th electron, and a strong deviation from its previously elliptical orbit The velocity acquired by the electron by virtue of its passage near the nucleus,

moreover, in large measure determines its principal quantum number, and it is in consequence much higher than if the electron were always to move at a large distance from the nucleus.

Whereas the classical theory required a simple relation to exist between the frequency of the electron in the atom and that of a spectral line, we find that, according to the quantum theory, no such direct relation exists between these two magnitudes, for the frequency of a spectral line is determined by the difference in the energy content of the atom in the respective stationary states (e g. between state 3 and state 2). But it is an interesting fact that, in spite of this, there exists a deep-seated *correspondence* between the rays emitted during the orbital transitions and the motion of the electron in the atom. This correspondence enables us to draw certain conclusions about the transitions from one stationary orbit to another and about the radiation sent out during these transitions These conclusions far transcend the results directly obtainable from the two hypotheses above-mentioned, and amongst other things, they have led to the views already referred to about the structure of the higher atoms.

4. The Origin of the Radioactive Rays

The α-rays, and to some extent also the β-rays, are derived from the nucleus of the disintegrating atom The first of these results follows particularly from the fact that the α-particle is a helium atom with a double positive charge, and that helium, like all material constituents of the atom, can only have been present in the nucleus. The conclusion that β-rays are also emitted by the nucleus is proved by the fact that the fundamental chemical and spectroscopic changes suffered by the atom in consequence of the emission of an α-particle $(+ +)$ can be completely annulled (see p 114) by the loss of two β-particles $(- -)$. This phenomenon admits of no other interpretation than that the α- and β-particles are derived from the same part, and thus the nucleus of the atom Nevertheless, only those β-particles that arise as a *direct* consequence of atomic disintegration have their origin in the nucleus The secondary β-rays, which are produced when primary β-, as well as α-, γ-, or other rays, traverse the atoms, originate in the electron cloud surrounding the nucleus, and thus have the same origin as those electrons that are involved during ionisation or other chemical processes.*

* Thus the β-rays emitted, together with α-rays, from radium, radiothorium, and from radioactinium originate exclusively in the electron shells of the atoms concerned (1) (See further on.)

The β-particles projected from the nucleus are subject to a retardation in their passage through the strong electric field of the outer electron cloud (2). The energy lost by the β-rays in this process reappears as electromagnetic radiation, in the form of soft γ-rays. Such soft γ-rays (e.g. those of the lead isotope RaB) can also be produced by the incidence of β-rays on lead, in which case they are none other than the characteristic rays of lead. The former are produced by the β-rays issuing from the nucleus of the RaB atom, whereas the latter are produced by the β-rays from an outside source. On the other hand, the harder γ-rays come from the nucleus itself, like the primary α- and β-rays emitted during radioactive disintegration. It has been found that in the disintegration of RaB or RaC, each disintegrating atom emits one γ-ray entity (impulse) (3).

The main evidence in favour of the nuclear origin of the harder γ-rays is that it enables us to give a simple and quantitative explanation of the *magnetic spectra of β-rays* (4). According to the above interpretation, β-ray spectra can, in general, be resolved into two parts ; one of these is of primary origin and is referred to the nucleus, whilst the other is of secondary origin and originates in the electron shells. Simultaneously with the emission of primary β-rays, primary γ-rays also issue from the nucleus, and the secondary part of the spectrum consists of β-particles liberated from the outer electron shells as the γ-rays traverse them. Let us first consider the limiting case, in which the magnetic spectrum of β-rays consists solely of primary lines, and is particularly simple Such a spectrum is met with in the case of UX, and in still purer form with ThC. Here the β-radiation should be accompanied by no γ-radiation, or only by a very small amount, and this is what we actually find. In the other limiting case, in which the β-spectrum consists exclusively of secondary lines, we should expect that every disintegrating atom emits γ-rays but no primary β-rays, i.e the atom does not suffer a β-transformation. Radiothorium supplies us with an instance of this kind ; it emits both α- and γ-rays, but does not undergo a β-transformation. Such a transformation would involve the production of an isotope of protactinium, for which there is absolutely no chemical evidence

A simple relation exists between the energy of the γ-impulse and that of the β-particles ejected from the electron groups. The latter amount is equal to the former reduced by the work that must

be performed to remove the electron from the group in question. This quantity of work will vary according to the electron group from which the electron is ejected.   Let us again consider the very simple spectrum of radiothorium , here we find two lines corresponding respectively to velocities of 0·51 and 0·47 of the velocity of light, so that the difference between the energies of the two lines is 0·2215 . 10^{-7} ergs   But this quantity of energy is none other than the difference between the works of separation of an electron from the M_1- and the L_1-groups of the element thorium, which is isotopic with radiothorium   The work of separation of an electron from the different groups is known from the results of Röntgen spectroscopy (cf. p. 55)   Thus the electron groups have been identified, from which the γ-ray emitted by the radiothorium nucleus is able to remove electrons, and the possibility of calculating the wavelength of the γ-ray presents itself, for the determination of which we possess no other methods (cf. p. 45).   The first mentioned line of the β-spectrum corresponds to an energy of 1·298 . 10^{-7} ergs, whereas the work of separation of an electron from the M_1-group is 0·0527 10^{-7} ergs, so that the sum of these two quantities ($= 1·3507$. 10^{-7} ergs) gives the energy of the γ-ray. The same result is also given by the sum of the energies of the second line of the spectrum and the work of separation of an electron from the L_1-group, i e by 1 0765 . $10^{-7} + 0·2582$. $10^{-7} = 1·3347$. 10^{-7} ergs The mean of these two almost equal values of the γ-ray energy corresponds to a wavelength of 1·46 . 10^{-9} cm , but it should be remembered that the accurate determination of the energy of the β-lines involves great experimental difficulties

If we now turn our attention to other radio-elements, e g. ThB, the spectrum of which comprises both primary and secondary constituents, it can be shown by similar considerations that the line of velocity 0 630c is derived from the K-group, and that of velocity 0 714c from the L_2-group, and that the γ-radiation concerned in producing these lines has a wavelength of 5·2 10^{-10} cm.

It does not always suffice, as in the above cases, to assume only *one* type of γ-ray in order to explain the β-spectrum , for instance, in the case of RaB the presence of six γ-ray types has been established. Also when α-rays leave the nucleus γ-radiation is emitted, but it is usually only of small intensity.

The regularities in the differences between the γ-rays emitted by the nucleus are reminiscent of the regularities shown by series

spectra. These are explained (see p. 80 ff.) by assuming that we are here dealing with transitions of an electron from one stationary orbit to another. This suggests that even in the nucleus of an atom there are different energy levels, in which case we should attribute the emission of γ-rays from the nucleus to transitions of an electron in the nucleus from one level to a more deeply seated one

The following Table XV gives a number of the wavelengths of the γ-rays which have been evaluated by the above method (5).

TABLE XV
Wavelengths of γ-Rays

Radioactive Substance.	Type of Disintegration	Wavelength of the γ-Rays
Radium - - -	α-radiation	$6\,6\quad 10^{-10}$ cm
Radium B - -	β-radiation	$2\cdot3\quad 10^{-9}$
		$5\,13\quad 10^{-10}$
		$4\cdot80\quad 10^{-10}$
		$4\cdot20\quad 10^{-10}$
		$3\,52\quad 10^{-10}$
Radium C - -	β-radiation	$4\,53\quad 10^{-10}$
		$3\cdot75\quad 10^{-10}$
		$3\cdot20\quad 10^{-10}$
		$2\cdot04\quad 10^{-10}$
Radium D - -	β-radiation	$2\,7\quad 10^{-9}$
Thorium B - -	β-radiation	$5\,2\quad 10^{-10}$
		$4\cdot16\quad 10^{-10}$
Thorium C″ - -	β-radiation	$4\,55\quad 10^{-10}$
		$2\cdot43\quad 10^{-10}$

We shall now briefly compare the production of the characteristic Röntgen spectrum with that of optical series spectra, in the light of the atomic model already described   We have seen that the optical spectrum of an element arises when an electron of the outer shell of the atom passes over from one to another possible orbit. The production of the Röntgen spectrum, on the other hand, is caused by the sudden change in position of electrons in the inner layers, i e. those lying next the nucleus.   The action of the nucleus on these electrons is so vastly greater than that of the outer electrons, that to all intents and purposes, it alone calls for consideration.   It is due to this circumstance that simple relationships are found to hold between the characteristic Röntgen spectra of the elements and their atomic numbers.

On the other hand, those processes that take place in the outer layers of the atom, i e. more distant from the nucleus, are hardly subject to the direct action of the nucleus, and for this reason we do not in this case find any simple relation between the nuclear charge number and the optical spectrum   The latter is determined chiefly by the position of the element in its group in the periodic classification , for instance, the spectra of the alkalies show essentially the same structure, in spite of their greatly differing atomic numbers, because the peripheral arrangement of their electrons is the same

One of the most striking differences between Röntgen and optical rays lies in the fact that no absorption lines occur in Röntgen radiation. If, for instance, we pass white light through sodium vapour, the characteristic D-line of sodium is strongly absorbed by the vapour. With Röntgen lines there is no analogy to this behaviour , the K_a-line of an element is no more strongly absorbed by a layer of the same element than are the lines of slightly greater or lesser frequency   Not until much shorter wavelengths have been reached do we find a sudden increase in the absorption, and simultaneously we find that the K_a-line is now emitted by the layer . In optics, fluorescent substances show a similar behaviour, in that they convert light of shorter into light of longer wavelength, and for this reason the characteristic Röntgen radiation of the elements is also sometimes called " fluorescent radiation "

On the basis of the current model of the atom, we can readily understand the difference in behaviour   In order to produce a Röntgen absorption line, we must remove an electron from one of the inner orbits of the atom to one more remotely situated , but all the inner electron groups are completely occupied by electrons, and only when the energy of the incident waves is sufficient to remove the electron to the periphery of the atom is it possible to have absorption. In contrast to optical absorption spectra, for the production of which outlying electrons only need to be slightly raised in level, we require a much shorter wavelength than that corresponding to the emission line, in the case of Röntgen rays, in order to supply the necessary energy   But once an electron has been removed from the innermost orbit to beyond the limits of the atom, in the manner described above, it is then possible for an electron from the successive second, third, etc , orbits to spring into the resulting gaps, and the K_a-, K_β-, etc., emission lines then make their appearance.

PLATE II

$\lambda = 1532 \times 10^{-11}$ cm

FIG. 24 (p 77)
Absorption Spectrum of Holmium in the L-Region

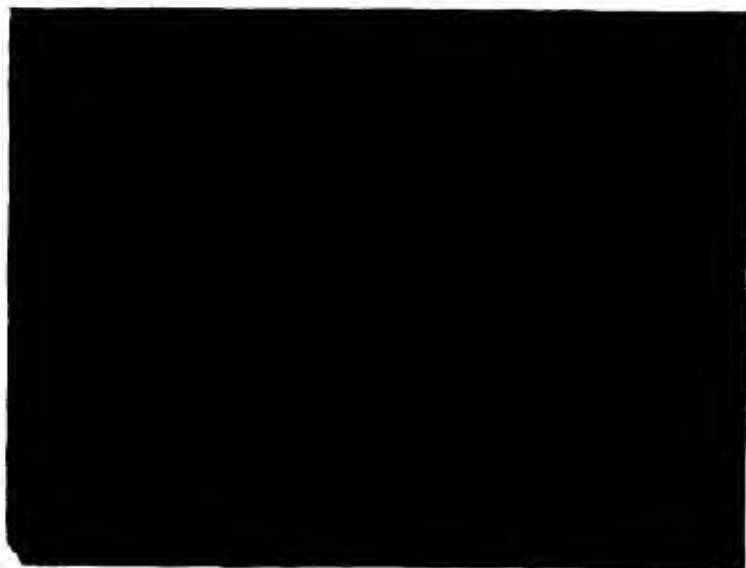

FIG 25 (p 78)
Tracks of α-Particles

Fig. 24 (Plate II) shows a part of the absorption spectrum of holmium in the L-region.   On the right-hand side the emission lines of tungsten are photographed, and on the left-hand side the heterogeneous radiation of the tungsten anti-cathode, in the path of the rays of which a thin layer of a salt of holmium has been introduced. We can detect the increased absorption in the holmium, which sets in at a wavelength of $1532\ 2\ 10^{-11}$ cm , corresponding to the LIII edge, and proceeds in the direction of shorter wavelengths.   Such " absorption edges " enable us to determine the " levels " of a series, mentioned on p. 67.

5. Scattering of the Rays in passing through Atoms

As is clear from the above sketch of the theory of the atom, the passage of material particles through atoms is rendered possible by the fact that the impenetrable atomic nucleus only occupies an infinitesimally small part of the atomic volume, whereas the remainder of the space can be penetrated.   But the projected particle must have sufficient kinetic energy to penetrate through the outer mantle of the atom   Hence, like the very rapidly moving α-particles, even recoil atoms and material particles that have received sufficient impetus in a positive ray tube are able to traverse other atoms

Thus, for example, if an α-particle passes through the atoms of a piece of gold foil, it will pass between the surface of the atom and the atomic nucleus, and approach the nucleus more or less closely. In view of the relatively very large intermediate space, it will only very occasionally reach the immediate neighbourhood of the nucleus, and we are able to apply calculations to such rare occurrences.   But when the particle does approach very close to the nucleus, it will experience a strong deviation from its rectilinear path, because both the nucleus and the α-particle are positively charged ; in other words, as discussed on p 28, the particle will be scattered (6) by an amount dependent on the nearness of approach   Experiments on scattering have shown that Coulomb's law retains its validity down to a distance of about $5 \cdot 10^{-12}$ cm from the centre of heavy atoms, and in the case of collisions between the nuclei of hydrogen and helium the corresponding distance is as small as $5 \cdot 10^{-13}$ cm. In any case, the exponent in the formula for the law of force, should it differ at all from 2, must lie between the limits of $1\ 97$ and $2 \cdot 03$. This phenomenon of the scattering of a rectilinear pencil of rays can

only be explained by the existence of a strong electric field within the atom, and the study of it was therefore of the utmost importance in the investigation of atomic structure, and in particular for the estimation of the magnitude of the nucleus and the nuclear charge number.

But apart from the influence of the nucleus of the atom penetrated, the α-particles also suffer scattering by the extra-nuclear electrons in the atom. Thus, during their passage through the atoms, the individual α-particles encounter a somewhat varying number and arrangement of electrons, and their respective losses in energy are not all the same, so that this manifests itself as a scattering of the particles The scattering produced by the electrons is much smaller than that due to the nuclei, but still, the value found experimentally is appreciably in excess of that to be expected theoretically (7)

In consequence of their smaller mass, β-particles exhibit the phenomenon of scattering (8) to a much higher degree than α-particles.

It has been possible to record photographically this difference in the behaviour of the radioactive rays in their passage through air (9) Figures 25 to 27 show photographs of this kind, which have been taken by the method outlined below (Plates II and III)

The condensation of a super-saturated vapour takes place where nuclei of condensation are available One of the most effective methods of producing condensation nuclei is by the formation of ions in the gas Now since ions are produced along the tracks of the radioactive rays, it follows that, if such rays pass through supersaturated water vapour, droplets of water will be deposited along their path, and if the illumination be suitably chosen, the tracks of the particles will be visible

Fig 25 (Plate II) shows the tracks of individual α-particles. Almost without exception they are rectilinear, and the ionisation produced by the rays ceases quite suddenly, which indicates that they have a definite range (10) The sudden bend near the end of the track, which can be seen in a few cases, is caused by the phenomenon of nuclear scattering already discussed. In certain cases, photographs have been obtained which show forked tracks, one of the branches being due to the deflected α-particles, and the other to the track of the recoiling atom responsible for the scattering.

The tracks of swift and slow β-particles are well shown in Fig 26

PLATE III

FIG 26 (p 78)
Tracks of β-Particles

FIG 27 (p 79)
Tracks of α-Particles from ThC

(Plate III).   In the former case they are often straight over many
centimetres, whereas in the latter the deviations due to simple or com-
pound scattering are very marked.   The increase in the ionisation of
β-particles as the velocity diminishes is also revealed in an increasing
density of the tracks near the end of the range (cf. p. 38) (*11*)

On p 21 it was mentioned that one in eleven thousand of the
α-particles (R = 8·6 cm) from ThC has a range of 11 5 cms.   Such
α-particles of long range from ThC are shown in Fig. 27 (Plate III).
projecting well beyond the main beam of the rays   A particle of
range 9·3 cms is also discernible (*12*).

A further method which allows us to observe the trajectory of
individual α-particles is that in which the rays strike a thin section
of willemite (see p. 195) at grazing incidence (*13*)   The mineral must
be a sample which luminesces brightly   If we make use of the rays
from polonium, for example, we then observe short luminous tracks
of about 0·02 mm in length, this distance corresponding to the range
of the α-rays in willemite

We can also photographically register the tracks of recoil atoms.
They appear as a continuation of the track of the α-particle in the
reverse direction from the origin of the rays, and attain a length of
only 1·5 mm (*14*).

When Rontgen rays are scattered by a light substance such as
graphite (*15*), they can be divided into two parts, one of which
possesses the same wavelength as the primary rays, whereas the
other has a somewhat greater wavelength (cf p 50)   The scattering
without change in wavelength is produced by a fairly large number
of electrons, whilst that accompanied by a change in wavelength is
caused by a single electron   In the latter case the scattering electron
suffers recoil, and thereby takes up a part of the energy quantum of
the Rontgen ray ; thus the energy quantum of the scattered ray
must be smaller, and the wavelength of the ray correspondingly
longer than that of the primary ray.   If the scattering is caused by
an appreciable number of electrons, the total mass of which is
relatively large, the quantity of energy removed from the Röntgen
rays by recoil is insignificant. and the wavelength of the scattered
rays is identical with that of the primary rays.

The main features of the absorption and scattering of γ-radiation
may be described in the following manner.   When γ-rays traverse
matter, the characteristic radiations of the absorbing medium are
excited.   The atomic absorption coefficient of the fluorescent

radiation varies as the cube of the wavelength of the incident radiation, and as the fourth power of the atomic number of the absorber. The pure atomic absorption coefficient of scattering is proportional to the atomic number of the absorber. For light elements, the absorption is almost wholly due to scattering.

6. MATHEMATICAL APPENDIX TO THE CHAPTER ON ATOMIC STRUCTURE *

Let us consider the motion of an electron and of a positive nucleus, the mass of which can be assumed to be indefinitely large, and for purposes of simplicity let us restrict ourselves to circular orbits

By Coulomb's law, the force of attraction between the nucleus of charge Ne and an electron of charge e amounts to $\dfrac{Ne^2}{a^2}$, whilst the equal but oppositely directed centrifugal force has the value $\dfrac{mv^2}{a}$, where m denotes the mass of the electron, v its velocity, and a the radius of the electron orbit. Such an atom, constructed after the manner of a planetary system, will hold together when

$$\frac{Ne^2}{a^2} = \frac{mv^2}{a} \qquad\qquad (1)$$

The theory of series spectra requires that the angular momentum mva of the electron in the stationary orbits cannot assume arbitrary values, but must always be an integral multiple of $\dfrac{h}{2\pi}$, i.e

$$mva = \frac{nh}{2\pi}, \qquad\qquad (2)$$

where n is a whole number.

By combining equation (2) with equation (1), we can calculate the radius of the orbit of the electron, its velocity, and also the work (W) necessary to separate the electron completely from the atom, i.e to remove it to infinity, or to " ionise " the atom. Moreover, we can also calculate from this the revolution frequency (ω) of the electron in its stationary orbit. We thus obtain

$$a = \frac{n^2h^2}{4\pi^2 Ne^2m}, \qquad\qquad \cdots \cdots \cdots \quad (3)$$

* This section is introduced into the text in such a way that even if it be omitted, the intelligibility of the remaining sections is not interfered with.

$$v = \frac{2\pi e^2 N}{hn}, \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots (4)$$

$$W = -\tfrac{1}{2}mv^2 + \frac{Ne^2}{a} = \frac{2\pi^2 e^4 m N^2}{h^2 n^2}, \quad \ldots \ldots (5)$$

$$\omega = \frac{4\pi^2 m e^4 N^2}{h^3 n^3}. \quad \ldots \ldots \ldots \ldots (6)$$

On the lines of the theory described, the emission of spectral lines takes place when the electron jumps from one of the orbits permissible by the quantum hypothesis into an orbit of lesser energy situated nearer the nucleus, e g. from the n_1^{th} orbit to the n_2^{th} orbit. If v denotes the frequency of the spectral line, and W_n the energy content of the system in the state n, then

$$vh = W'_{n_2} - W_{n_1}. \quad \ldots \ldots \ldots (7)$$

For any arbitrary atom, we have

$$v = v_0 N^2 \left(\frac{1}{n_2{}^2} - \frac{1}{n_1{}^2} \right), \quad \ldots \ldots \ldots (8)$$

where $v_0 = \dfrac{2\pi^2 e^4 m}{h^3} = 109{,}740$ (Rydberg's constant) $\times 3 . 10^{10}$, and N is the atomic number of the element. For the frequency of the hydrogen lines (Balmer series) we obtain

$$v = v_0 \left(\frac{1}{n_2{}^2} - \frac{1}{n_1{}^2} \right) = (n_1 - n_2) v_0 \frac{n_1 + n_2}{n_1{}^2 n_2{}^2}. \quad \ldots \ldots (9)$$

When n_1 and n_2 are large as compared with their difference, we can put $n_1 = n_2 = n$ in the last factor, and by taking account of equation (6) we obtain for the frequency $v = (n_1 - n_2) \times \dfrac{2v_0}{n^3} = (n_1 - n_2)\omega$.

From this we see that there exists in the region of large values of n a quantitative relation between the revolution frequency and the frequency of the radiation, i.e. a *correspondence* between the latter and the motion of the electrons in the atom in the region of large quantum numbers. The harmonics in the radiation, corresponding to $(n_2 - n_1) > 1$, however, are only present when the motion of the electron is elliptical, and not when it is circular.

VIII

APPLICATIONS OF THE THEORY OF DISINTEGRATION

1. The Fundamental Assumption

THE theory of radioactive disintegration is based on the single assumption that the number of atoms of a radio-element disintegrating at any instant is always proportional to the number of atoms of that element present.

If we have 10^{11} atoms of a given radio-element and 1000 of these disintegrate in a given interval of time, then if we only had 10^{10} atoms of the same radio-element, the number disintegrating in the same time would be 100, and so on. The factor of proportionality, or the so-called *disintegration constant* (λ) is found to be a quantity which is completely independent of all outside conditions such as temperature, pressure, etc., and characteristic solely of the disintegration process under consideration.

Only rarely does disintegration lead directly to a stable product; in most cases the disintegration of an atom is followed by a whole series of successive transformations. The conditions in such a case are often very complicated, but the theory of transformation enables us to interpret them quantitatively, and to calculate the number of atoms of each intermediate product present at any time, provided that the disintegration constants are known. It also indicates means of determining the disintegration constants when these cannot be directly determined.

In what follows, we shall deal with the theory of transformation in a few typical cases of successive processes of disintegration

2. Production of a Substance of Short Life from a Parent Substance of Long Life Separation and Decay of UX

If we investigate the behaviour of uranium nitrate or of any other uranium salt, we find that it emits β-rays in addition to α-rays. In this connection we may recall that the radioactivity is a property of the uranium atom, and hence is entirely independent of the state of

combination of the element.   If we submit the uranium salt to a
process of crystallisation or to another process of chemical separation,
we find that the strength of the α-radiation from the substance is
unaltered, but that the β-radiation has been influenced.   It is
possible, e g. by the addition of an iron salt to the solution of the
uranium compound and later precipitation of the iron by means of
ammonium carbonate, to separate the β-rays completely from the
uranium   But these are now emitted with the same intensity from
the precipitated iron salt.   From this we may conclude that the
β-radiation has its origin not in the uranium, but in a radioactive
product separable from uranium, and known as uranium X.

The β-radiation of the iron salt does not remain constant, but
decreases exponentially , * viz. after the lapse of about 24 days it
has already sunk to one half of its original intensity, after 48 days
to one quarter, in 72 days to one eighth, and so on   One of the chief
characteristics of exponential decay is that, strictly speaking, the
disintegration is not completely finished until after an infinite period
of time.   But since the quantity and hence also the radiation of UX
sinks to about $\frac{1}{1000}$ of its original value after an interval of about
10×24 days, it follows that, for practical purposes, and provided it
were not too strong, we can assume the preparation to have com-
pletely decayed after this time (the ten-fold half-value period).†   It
is owing to this characteristic of the exponential decay curve that we
always consider the " *half-value period* " (T) of a radio-element,
i e. the time during which one half of the amount initially available
decays, instead of the absolute life period of the preparation
Although the latter quantity is always infinite theoretically, it is
finite for practical purposes, but it depends on the strength of the
preparation concerned and on the sensitiveness of our measuring
instruments, whereas the half-value period does not

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* Such a process is represented mathematically by the formula $N_t = N_0 e^{-\lambda t}$,
where N_0 is the number of atoms initially present, and N_t the number present
after a time t; λ is the disintegration constant, and e is the basis of natural
logarithms.   Here it is assumed that the intensity of the measured radiation is
always proportional to the number of atoms disintegrating in the unit of time.

† The radioactive substance can be detected for a longer period when we
use more sensitive instruments towards the end of the measurement than at
the beginning.   The range of measurement over which one and the same
instrument can be utilised rarely exceeds 1 · 1000 ; hence by means of such an
instrument the active preparation will be no longer detectable after a period
of magnitude ten times the half-value period.

Apart from the half-value period, we also make use of a quantity which is proportional to it, viz. the " *period of average life* " (τ). This concept is here defined analogously as in statistics. We multiply every life period by the average number of individuals that attain, but do not survive this period, and divide the sum of all these products by the total number of individuals. It can readily be shown mathematically that the period of average life (τ) so defined is equal to $\frac{1}{\lambda}$, the reciprocal of the disintegration constant λ, whereas the half-value period $T = \frac{1}{\lambda} \log_e 2 = \frac{0\ 69}{\lambda}$ * Thus in the case of UX, the disintegration constant $\lambda = 0\ 0290$ day^{-1}, and $\tau = 34\ 4$ days, from which $T = 23\ 8$ days

The variation of the activity of UX separated from uranium, as a function of the time, is shown in curve B of Fig 28, and this curve at the same time shows the proportional decrease in the number of UX atoms, on which the activity depends

3. The Production of UX from Uranium

We shall now again turn our attention to the uranium preparation from which we have supposed the UX to have been removed, and which therefore no longer emits β-rays It is found gradually to emit β-rays again, and after the course of 24 (more exactly 23 8) days it exhibits just one half of the β-radiation that it had before the separation of the UX After 2×24 days it has reached $\frac{3}{4}$, after 3×24 days $\frac{7}{8}$ of the value last referred to, etc. Moreover, this rise also takes place exponentially, and is graphically represented by the curve A of Fig. 28 Just as the complete decay of the separated

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* The half-value period is the time after which $N_t = \frac{N_0}{2}$; and since $N_T = N_0 e^{-\lambda T}$, we must have $\frac{N_0}{2} = N_0 e^{-\lambda T}$. From this follows $T = \frac{1}{\lambda} \log_e 2$. The definition of the period of average life given above can be expressed mathematically in the form

$$\tau = \frac{\int_0^\infty t \lambda N_0 e^{-\lambda t} dt}{N_0}, \text{ which is equal to } \frac{1}{\lambda}$$

Since $\tau = \frac{1}{\lambda}$, we can also define the period of average life as the time within which the whole material would disintegrate, if the number of atoms disintegrating per unit time were to remain the same as initially : for $\frac{N_0}{N_0 \lambda} = \frac{1}{\lambda} = \tau$.

UX is to be expected theoretically only after an infinitely long time, but is for all practical purposes already attained after 10×24 days, so also the β-radiation of the UX-free uranium preparation will have practically reached its original strength after 10×24 days, although theoretically this should require an infinite period of time. In Fig 28, the decay of the β-radiation of the separated UX, and the
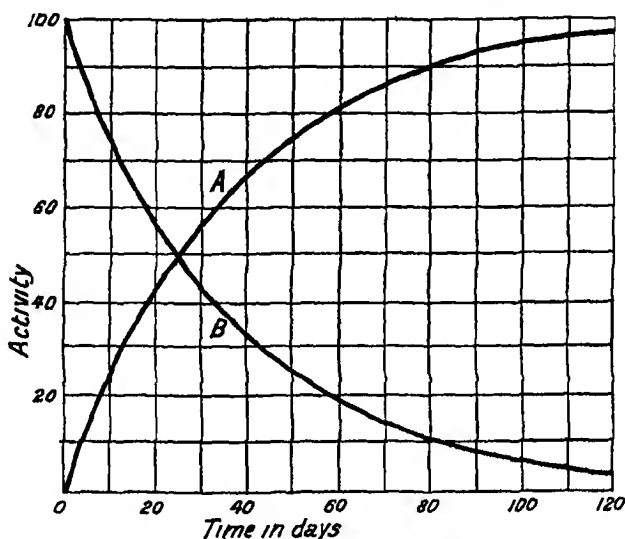

FIG 28   Growth (A) and Decay (B) of Uranium X

growth of the β-radiation of the uranium preparation are represented on the same graph From it we see that the *sum* of the two radiations, and hence the sum of the entire number of UX atoms present, is constant at every instant, and equal to the initial value before the separation of the UX.

4 RADIOACTIVE EQUILIBRIUM

The disintegration theory enables us to predict the behaviour described above, as will be clear from the following example.

We shall suppose that we have 10^{15} uranium atoms ($= 4 \cdot 10^{-7}$ gm.). Since the half-value period of uranium is approximately 10^{10} years (cf. p. 104), it follows that in 5 days, which we shall assume to be our unit of time, the relatively exceedingly small number of about 1000 atoms will disintegrate, or only the $10^{12\text{th}}$ part of all the available atoms. In the next 5 days the $10^{12\text{th}}$ part of the now

available atoms ($10^{15} - 1000$) will disintegrate ; but the difference between this number and 10^{15} is so vanishingly small that, even if we require a very accurate calculation, we can assume them to be' equal.   Thus in each of the succeeding periods of 5 days' duration we shall again find that 1000 atoms disintegrate.   Not until after the lapse of many thousands of years will the available amount of uranium have diminished appreciably, or the number of uranium atoms disintegrating in each period of 5 days be detectably different from 1000, and this period of time is far in excess of the time involved in our investigation of the behaviour of the short-lived UX.

Each 1000 disintegrating atoms have ceased to be uranium, by virtue of the disintegration ; they are now UX atoms, but only for a short time.   Since the period of average life of UX is only 34·4 days, about 15 % or 150 of the 1000 UX atoms will have already decayed after 5 days , of the remaining 850, 15 % will again decay in the next 5 days, or 127, a number appreciably different from 150, for there is an appreciable difference between the numbers 850 and 1000, and so on.   Thus in the course of 5 days the process of disintegration exercises a very strong influence on the amount of UX present, and hence also on the amount disintegrating.   The activity is proportional to the amount disintegrating at any moment, and thus our previous discussion makes it clear why the activity of uranium is practically constant, whereas that of the separated UX diminishes by about 15 % even after a period of 5 days.

Suppose we now consider how much uranium X would be formed if it were not separated from the uranium, but left to itself.   Whereas in each 5 days 1000 fresh UX atoms are always produced, independently of the number already present, the number of UX atoms disintegrating in the same time will be greater, the greater the number that have already been formed.   This behaviour necessarily leads to a condition in which, for a given interval of time, the number of UX atoms disintegrating will be equal to the number freshly formed, so that the quantity of UX actually present no longer increases.   This condition is called " radioactive equilibrium."   *A radio-element is in a state of radioactive equilibrium with its disintegration product, when the same number of atoms of the daughter element disintegrate as are formed in the unit of time.*   These important considerations will be quite clear from a study of Table XVI.

We see from the Table that the number of UX atoms disintegrating in the second interval of 5 days is almost double the number

TABLE XVI *

Number of time intervals of 5 days.	Number of UX Atoms produced in the Interval by the Decay of U Atoms	Number of UX Atoms available from the previous time-interval.	Sum of the Two Numbers	Number of UX Atoms decaying in the Interval of Time	Number of UX Atoms remaining at the end of the time-interval.
1	1000	—	1000	150	850
2	1000	850	1850	277	1573
3	1000	1573	2573	386	2187
4	1000	2187	3187	478	2709
5	1000	2709	3709	556	3153
6	1000	3153	4153	623	3530
7	1000	3530	4530	680	3850
8	1000	3850	4850	728	4122
9	1000	4122	5122	768	4354
10	1000	4354	5354	803	4551
.				.	
50	1000	5667	6667	1000	5667
51	1000	5667	6667	1000	5667
52	.	..	,	,,	.
53	.	.,	,	,,	,,

disintegrating in the first 5 days, whereas the difference between the numbers for the 10th and 9th intervals has already become small, and after about 50 time-intervals 1000 atoms decay in 5 days, or just as many as are produced. Thus the number of UX atoms remaining from the previous time-intervals remains constant at 5667, or in other words, radioactive equilibrium has been established. Fifty such time-intervals are 250 days, or approximately the ten-fold value of the half-value period of UX. We have already seen that this multiple of the half-value period suffices for the attainment of the maximum activity of a uranium preparation that has been freed from its UX, *i.e.* for the establishment of radioactive equilibrium.

In determining how much UX, or of another short-lived element, is present, it is usually sufficient to express the strength of the

* The numbers in the Table are not strictly correct, for during the time-unit of 5 days, which has been chosen on the grounds of clearness, the decay does not take place uniformly. A correct treatment presupposes that the time-unit can be neglected in comparison with the half-value period. The formulae of infinitesimal calculus operate with indefinitely small times, within which the decay is strictly constant.

preparation in relative current units (*e.g.* 50 scale divisions per minute with a given electroscope). We may, however, wish to express how much by weight of the short-lived element is present, this being always formed in quantities which are too small to be weighed This can be done most readily by utilising the conception of radioactive equilibrium. According to the basal assumption of the disintegration theory, the number of uranium atoms disintegrating per unit of time is equal to the product of the disintegration constant (λ_1) and the number of atoms available (N_1), or $N_1\lambda_1$ Similarly, for the number of UX atoms disintegrating per unit of time we obtain the product $N_2\lambda_2$, where N_2 is the number, and λ_2 the disintegration constant of the UX atoms. Now we have seen that in the state of radioactive equilibrium the number of UX atoms produced per unit of time is equal to the number disintegrating, and since the former number is equal to that of the uranium atoms disintegrating per unit of time, it follows that in the state of radioactive equilibrium

$$N_1\lambda_1 = N_2\lambda_2$$

Since the weight of a single uranium atom is known (238 times the weight of an atom of hydrogen $= 238 \times 1 66 . 10^{-24} = 3.96 . 10^{-22}$ gm.), we can evaluate N_1 by weighing the uranium λ_1 and λ_2 (see p 84) are known, and so we may directly obtain the required value of N_2 In 1 gm. of uranium, that has not been chemically treated for at least eight months, we have, for example,

$$N_1 = \frac{1}{3 96 . 10^{-22}} = 2 52 \quad 10^{21},$$

$$N_2 = 2 52 . 10^{21} \times \frac{\lambda_1}{\lambda_2} = \frac{2.52 \quad 10^{21} \times 4 9 . 10^{-18}}{3.4 \quad 10^{-7}} = 3 63 . 10^{10}.$$

Since 1 atom of UX weighs $234 \times 1.66 . 10^{-24} = 3 88 . 10^{-22}$ gm , the weight of the whole quantity of UX

$$= 3.63 . 10^{10} \times 3.88 \quad 10^{-22} = 1 4 \quad 10^{-11} \text{ gm.*}$$

It is possible to detect such a very small quantity with the aid of its β-radiation by virtue of the fact that UX disintegrates rapidly, and hence emits a relatively large number of β-rays. *The determining factor for the detection of an element by radioactive means is not*

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* If we neglect the difference in atomic weight of the two elements, we can also obtain an approximately correct value for the equilibrium quantity by inserting the amounts by weight directly, instead of the numbers of atoms N_1 and N_2.

the amount of it, but the product of the quantity and the disintegration constant.

• When several radioactive substances are in radioactive equilibrium, it follows immediately from the above considerations that each of the substances emits exactly the same number of α-particles per unit of time, provided each emits α-rays. More generally, we say that the same number of atoms of each of the substances in equilibrium is transformed in the same interval of time. Nevertheless, the ionisation produced by the rays from each substance shows slight differences in the various cases, owing to the different ranges of the α-rays (*e g.* see p. 22)

5 CASE WHERE THE LIFE OF THE PARENT SUBSTANCE IS NOT MUCH
   LONGER THAN THAT OF THE DAUGHTER ELEMENT THE ACTIVE
   DEPOSIT OF THORIUM

Whereas the life period of uranium is so large that the quantity of it remains practically unaltered during the time it requires to establish radioactive equilibrium with its daughter element, in many cases, *e.g.* in the formation of ThC from ThB, the quantity of the parent substance varies appreciably during the production of the daughter element

The transformation last mentioned also differs from that of uranium in other important points   Uranium is available in weighable quantities, and the separation of its transformation product is carried out by ordinary chemical methods , every method that is suitable for the separation of thorium from uranium is also applicable to the separation of UX (see p. 174)   In the case of ThB and ThC, however, we have to do with a parent substance present in unweighable quantities, and in the form of the so-called *active deposit,* which has to be collected by a method quite new to chemistry.

As already mentioned (p 2), one of the disintegration products of the radium, thorium, and actinium disintegration series is a gaseous substance, the so-called " emanation " The emanation of thorium decays with a half-value period of 55 seconds, and the atoms of ThA and the succeeding products formed are all metallic ; the charged particles formed by the aggregation of such atoms are held in suspension in the air for a lengthy period, in consequence of their smallness, and are only deposited gradually on the surrounding surfaces.   These disintegration products of the emanation in their turn decay with appreciable rapidity, and are thus strongly active,

and it is for this reason that the invisible deposit which they form on the surrounding surfaces is called the *active deposit.** As a consequence of their mode of production, the particles carry a positive charge (cf. p. 60) ; this property supplies us with a means of preventing them from being deposited in the direction of the force of gravity.   By introducing a negatively charged surface, *e.g.* a platinum wire at a potential of −100 volts, into the space in which the emanation decays, and in which the particles are in suspension, the active deposit can be collected upon it.

Fig 29 represents an arrangement by means of which the active deposit may be accumulated and collected

The metallic base and the walls of the vessel are connected to the positive pole of the battery, and the platinum wire *W*, which passes through the insulating bung of the vessel, is connected to the negative pole   If we introduce a thorium preparation *D* into the vessel, and do not remove the platinum wire until after the lapse of several days ("long exposure"), we find that it emits α-, β-, and γ-rays, and

FIG 29   Apparatus for Collecting the Active Deposit

that its activity decreases with a half-value period of 10·6 hours, independently of which of the types of rays we may consider.   This is illustrated by curve *B* of Fig 30 †

Suppose we now repeat the experiment, but take only a "short exposure" of a few minutes   We find that the wire now shows no initial α-activity after its removal from the experimental vessel , but it gradually acquires such an activity, the increase taking place in accordance with curve *A* in Fig 30

After about 4 hours the curve reaches a maximum value, and the activity then decreases just like that for a long exposure, with a half-value period of 10·6 hours.

* Since the active deposit exists on the surface of bodies in contact with which the emanation has decayed in the form of an exceedingly fine and loose deposit, it can readily be transferred to other bodies, whereby they acquire an " induced " activity.   Before the material nature of the active deposit had been recognised, it was customary to call the activity acquired by bodies that had been in contact with emanation by the name " induced activity."

† The slower decay of the curve *B* during the first hour or two is due to the fact that the state of " transient equilibrium " between ThB and ThC is only gradually established (see p. 98).

The most obvious explanation of this behaviour is that the substance (called ThB) which is collected on the platinum wire does not itself emit α-rays, but that these are emitted by the succeeding product ThC. The α-activity of the wire thus increases in the same measure as ThC is gradually formed from the disintegration of ThB. This process is continued until radioactive equilibrium has been established between the two substances, and thenceforward the variation with time of the activity of the platinum wire is just the same as if we had been dealing with a long exposure.
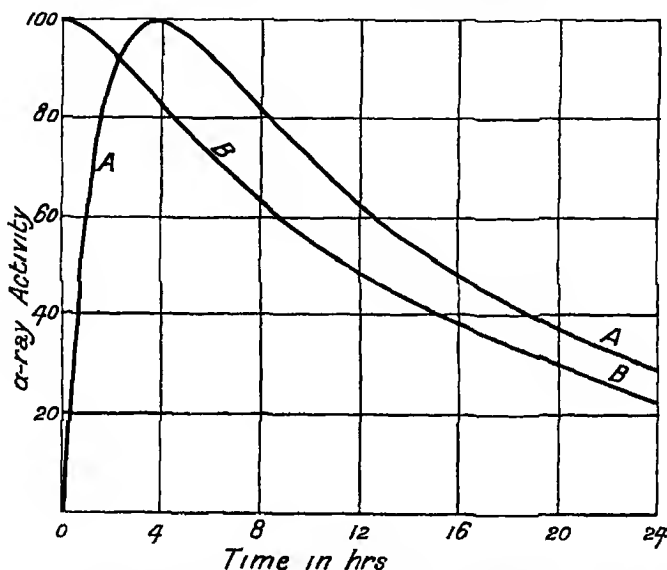
FIG 30   Variation with Time of the Activity of the Active Deposit of Thorium, after a short (A) and after a long (B) exposure to emanation

The measurement of the β-activity of a platinum wire exposed to emanation for a short time gives support to the above conclusion. This activity is present right from the beginning, which shows that ThB is a radio-element that emits β-rays

From the fact that radioactive equilibrium between ThB and ThC is established after a few hours, it can be concluded that the half-value period of the latter is about one hour. The accurate value for T (= 60·8 minutes) can be calculated from the equation for the curve, or it may be obtained by the preparation of pure ThC and the determination of its decay curve. Thus, if we immerse a small nickel plate in a hydrochloric acid solution of the active deposit, it

is found that ThC accumulates on the plate, and that it is practically free from ThB. By following the diminution in intensity of the α-activity of the separated ThC, we obtain the same value for T as by the calculation referred to above.

" Short " and " long " exposures are limiting cases , for example, if we expose our platinum wire to emanation for an hour, the α-activity still increases initially, but instead of starting from zero it commences at a value intermediate between zero and the maximum value of the α-activity In all cases, however, after radioactive equilibrium has been established for some time, the activity diminishes with the half-value period of ThB. The parent substance of longer life gradually impresses its period on the daughter element.

Such a behaviour can be readily understood when we consider that in the state of equilibrium just as many ThC atoms disintegrate in unit time as are produced in the same time , but the latter number is also equal to the number of ThB atoms disintegrating, and since this is proportional to the total number of available ThB atoms, it follows that the number of ThC atoms disintegrating—for this determines the α-activity—will be proportional to the total number of available atoms of its parent substance

The behaviour just described is often met with in radioactive analysis. When emanation is in equilibrium with radium, it disintegrates exceedingly slowly with the period of radium, although the half-value period of the emanation is only 3 81 days Polonium $(T = 136$ days), in equilibrium with RaD, disintegrates with a half-value period of 16 years When the half-value period of the daughter element is only slightly smaller than that of the parent element, the regular decay with a half-value period equal to that of the parent element does not arise until the lapse of a more or less lengthy period after the attainment of the maximum activity. For example, the activity of RaC $(T = 19\cdot5$ minutes), after the maximum activity has been reached, diminishes with a half-value period of more than 30 minutes for a protracted period, instead of with the half-value period of RaB $(T = 26\ 8$ minutes) Moreover, since the behaviour of the active deposit of radium is on other grounds more complicated than that of the active deposit of thorium, we shall deal with it independently.

6. THE ACTIVE DEPOSIT OF SHORT LIFE IN THE CASE OF , RADIUM

Thorium emanation is not directly transformed into ThB. Between these two elements there exists an intermediate product, ThA (see p. 187), which could be left out of the above discussion, however, owing to its very short period ($T = 0\,14$ second). This cannot be done, however, in the case of the corresponding radium products RaA has a half-value period of 3 05 minutes, a value which, compared with that of RaB (26 8 minutes) and RaC (19·5 minutes), is too great to be neglected Thus the α-activity of a platinum wire that has been given a long exposure of about 5 hours in radium emanation decays in the manner indicated by curve I in Fig 31 From this we see that it decays rapidly at first, and then
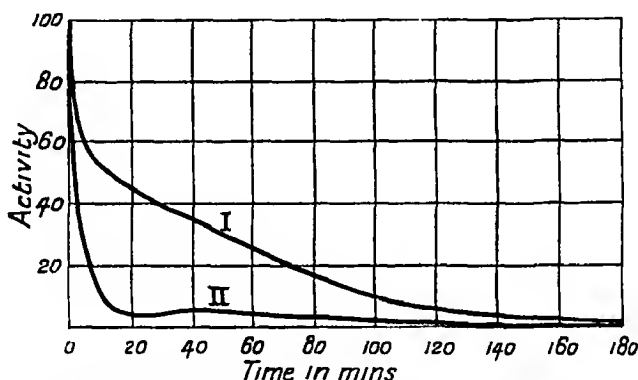
FIG 31   Variation with Time of the Activity of the Active Deposit of Radium, after a long (*I*) and after a short (*II*) exposure to emanation

more and more nearly with the period of RaB After a short exposure of only a few minutes, on the other hand, it decays very rapidly at first, with the period of RaA, as represented by curve II in Fig. 31. Then for some time it remains practically constant, for in this region the RaA has almost completely disintegrated; but almost in the same degree as its ionising action ceases, the activity of the succeeding RaC increases, for it is being gradually formed, and likewise emits α-rays. Before the RaC has attained equilibrium with the RaB, the RaA has completely disintegrated, and thenceforward similar conditions apply to those met with in the thorium series.

7. PRODUCTION OF AN ELEMENT OF LONG LIFE FROM ONE OF SHORT
   LIFE. THE ACTIVE DEPOSIT OF ,LONG LIFE OBTAINED FROM
   RADIUM

Whereas the active deposit of thorium leads to a product which is at least practically stable, or completely inactive, in the case of the active deposit of radium we can detect a residual activity after the lapse of a few weeks, *i e* after the RaA, RaB, and RaC have completely disintegrated. Moreover, this activity continuously increases for a relatively long period of time. From the disintegration of the short-lived RaC the long-lived product RaD is formed, for which $T = 16$ years. The disintegration of this element leads by way of two further active products (RaE, $T = 4.85$ days, and RaF, $T = 136$ days) to the stable end-product RaG. In the case of radium, the elements RaD, RaE, and RaF (the last also known as polonium) are called the " active deposit of long life." *

RaD is a β-rayer, and its radiation can only be detected with difficulty, so that this is not suitable for the detection of the quantities of RaD available   On the other hand, the succeeding product RaE emits β-rays that can be readily detected, and they can be made use of for the identification and quantitative evaluation of the available quantities of RaD, in much the same way as we can utilise the a-radiation of ThC for the identification of its parent substance ThB. In the detection of the amount of RaD present, we also frequently revert to the a-radiation emitted by the third member of the long-lived active deposit, viz RaF or polonium.†

If we collect the active deposit of thorium in the manner described, we shall arrive at the practical maximum of activity attainable in about 3 days, and in the corresponding case of the short-lived active deposit of radium in as short a period as 5 hours. In the case of the long-lived active deposit of radium, however, we should have to collect it for over 100 years, in order to reach its greatest possible activity. During this time, however, the quantity of radium in our activating vessel, which is the source of the emanation and the

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* The reason why we can only gradually detect the long-lived active deposit of radium by electroscopic or photographic means is to be found in the extreme softness of the β-rays from RaD, which is almost inactive.

† The element RaE, which comes between RaD and RaF, can often be left out of account in these measurements, owing to its relatively short half-value period.

active deposit, will have diminished, whereas we have been able hitherto to regard it as stable ($T = 1580$ years).   In consequence of this, it can be shown that after the lapse of 110 years the number of RaD atoms produced from a given quantity of radium will already have begun to diminish.

It follows from the above considerations that, when we prepare the strongest RaC preparation possible after an exposure of several hours, we should by no means obtain a strong RaD (or RaF) preparation as a result of its decay.   Large quantities of RaD can only be accumulated by the utilisation of extended intervals of time, e g. on the walls of a closed vessel in which a large quantity of radium emanation has disintegrated, or in radium preparations sealed off in glass tubes, or in minerals, etc   The quantity of RaD in equilibrium with 1 gm of radium amounts to about 10 mg.

IX

MATHEMATICAL TREATMENT OF DISINTEGRATION PROCESSES.*

ALTHOUGH the analysis of radioactive processes can sometimes be performed graphically, in most cases we have to revert to calculation. In this chapter we shall therefore briefly discuss the mathematical treatment of a few of the most important disintegration processes.

1. DISINTEGRATION OF A PURE SUBSTANCE

According to the fundamental assumption of the disintegration theory, the number of atoms disintegrating in unit time is proportional to the number of atoms available at the instant considered. From this it immediately follows that, if N_0 atoms are present initially, only $N_t = N_0 e^{-\lambda t}$ atoms will be available after a time t, where λ is the disintegration constant and e is the basis of natural logarithms (cf p. 83).

Example. Suppose that there are 1000 relative units (*e.g.* scale divisions per minute, measured with an a-electroscope) of ThB originally present. The number of units remaining, after the course of 1 hour = 3600 seconds, will be $1000 \cdot e^{-1.82 \cdot 10^{-5} \times 3600} = 937$, since $\lambda = 1.82 \cdot 10^{-5}$ sec $^{-1}$

2. PRODUCTION OF A PURE SUBSTANCE FROM A CONSTANT PARENT ELEMENT

If we wish to calculate the growth of the daughter element, or the fraction of the maximum quantity N, obtainable, after the lapse of the time t, we apply the formula ·

$$N_t = N \, (1 - e^{-\lambda t}).$$

This expression follows immediately from the reciprocal nature of the growth and decay curves (cf. p. 85).

Example: Suppose we have mesothorium in equilibrium with all of its disintegration products up to and including ThA, so that

* What we said of Section 6 in Chapter VII also applies to this chapter (see p. 80).

we may regard the immediate parent of ThB as being constant in amount ; then if the maximum amount of ThB obtainable from this preparation after an " infinitely " long exposure amounts to 1000 relative units, we should have, after an exposure of one hour,

$$N_t = 1000 \ (1 - e^{-1\,82 \ 10^{-5} \times 3600}) = 63 \text{ units.}$$

3. From a Substance I, of which there are initially ($t=0$) A Atoms present, the Elements II, III, etc., are successively formed

We shall represent the numbers of atoms of the elements II, III, etc., by the letters B, C, etc   We require to find the magnitudes of A, B, C, etc., at a particular instant of time.   Suppose we expose a platinum wire in radium emanation for a short time, during which practically only RaA is deposited.   We measure its initial activity (=amount of RaA), and calculate how many of the RaB and RaC atoms formed from the RaA will be present after the lapse of the time t.   The number of atoms of RaB will be

$$B = A_0 \frac{\lambda_1}{\lambda_B - \lambda_1} (e^{-\lambda_B t} - e^{-\lambda_1 t}),$$

and of RaC,

$$C = A_0 \left\{ \left[\frac{\lambda_1 \lambda_{11}}{(\lambda_{11} - \lambda_1)(\lambda_t - \lambda_1)} \right] e^{-\lambda_1 t} + \left[\frac{\lambda_1 \lambda_B}{(\lambda_t - \lambda_{11})(\lambda_1 - \lambda_{11})} \right] e^{-\lambda_B t} \right. $$
$$\left. + \left[\frac{\lambda_1 \lambda_B}{(\lambda_1 - \lambda_t)(\lambda_{11} - \lambda_t)} \right] e^{-\lambda_t t} \right\},$$

where λ_A, λ_{11}, and λ_C are the relevant disintegration constants, and A_0 denotes the original number of RaA atoms present.

Thus, if there were 1000 atoms of RaA available at the time $t=0$, then after 10 minutes ($t=600$ sec) there would be 103 atoms of RaA, 756 atoms of RaB, and 124 atoms of RaC ; the remaining 17 atoms would have been already transformed into RaD.

4. At the Time $t=0$, we have Radioactive Equilibrium between the Transformation Products I, II, III, etc.

How many atoms of A, B, C, etc , will be present after a definite time t ?   This case corresponds to a long exposure in radium emanation, and we require to calculate the number of atoms of RaA, RaB and RaC still remaining on the platinum wire t minutes after its removal from the emanation.

H P R

Since radioactive equilibrium exists between the several products at the time $t = 0$, we must have

$$\lambda_A A_0 = \lambda_B B_0 = \lambda_C C_0 = n_0.$$

Thus if there were 1000 atoms of RaA present initially ($A_0 = 1000$), the initial numbers of atoms of RaB and RaC would amount to 8829 and 6395 respectively.

At the time t, the following numbers of atoms will be available :

$$A = \frac{n_0}{\lambda_A} e^{-\lambda_A t},$$

$$B = \frac{n_0}{\lambda_A - \lambda_B} \left(\frac{\lambda_A}{\lambda_B} e^{-\lambda_A t} - e^{-\lambda_A t} \right)$$

$$C = n_0 (a \ e^{-\lambda_A t} + b \cdot e^{-\lambda_B t} + c \cdot e^{-\lambda_C t}),$$

where

$$a = \frac{\lambda_B}{(\lambda_B - \lambda_A)(\lambda_C - \lambda_A)}, \quad b = \frac{\lambda_A}{(\lambda_A - \lambda_B)(\lambda_C - \lambda_B)}, \quad c = \frac{\lambda_A \lambda_B}{\lambda_C (\lambda_A - \lambda_C)(\lambda_B - \lambda_C)} \ ;$$

thus after 10 minutes we should have

$$A = 103, \quad B = 7543, \quad C = 6276.$$

5. "SECULAR" AND "TRANSIENT" RADIOACTIVE EQUILIBRIUM

In the previous example the equilibrium quantities of RaA, RaB and RaC have been calculated on the assumption that the emanation, from which the RaA is formed, remains constant in amount, *i.e.* is itself in equilibrium with radium. When this is not the case, as when the exposure is made in a vessel that contains only emanation, we are no longer justified, strictly speaking, in neglecting the rate of decay of the emanation, as compared with that of the short-lived active deposit   It is true that even in this case we obtain a state of equilibrium between the four products, but the relative quantities involved are somewhat different.   The balance is in favour of the later products, the decay of which cannot keep pace with that of the parent substance, so that it is not possible to attain " secular " equilibrium   This state, which is very often met with in practice, is called " transient equilibrium "   For instance, in the case of radium emanation, the quantities of RaA, RaB and RaC corresponding to transient equilibrium are about 0·05 %, 0·5 % and 1 % greater

respectively than those corresponding to the state of secular equilibrium. These numbers are calculated according to the formulae :

$$\text{For RaA,} \quad \frac{\lambda_A}{\lambda_A - \lambda_{Em}} ;$$

$$\text{For RaB,} \quad \frac{\lambda_A \lambda_B}{(\lambda_A - \lambda_{Em})(\lambda_B - \lambda_{Em})} ;$$

$$\text{For RaC,} \quad \frac{\lambda_A \lambda_B \lambda_C}{(\lambda_A - \lambda_{Em})(\lambda_B - \lambda_{Em})(\lambda_C - \lambda_{Em})}$$

From these formulae we see that the ratio of the equilibrium quantities corresponding to transient and secular equilibrium respectively will become unity, when the rate of decay of the parent substance can be neglected. The nearer this approaches to those of the succeeding products, on the other hand, the greater is the value of the ratio Thus for the products (ThB and ThC) which succeed ThX, the correction already amounts to from 13 to 15 %, when we are dealing with the decay of ThX which is not in equilibrium with the long-lived parent element radio-thorium.

X

THE TRANSFORMATION SERIES OF URANIUM, ACTINIUM AND THORIUM

THE investigation of the radioactive transformations on the basis of the disintegration theory leads to the result that all radioactive substances, with the exception of rubidium and potassium, the activity of which still requires further investigation, are products of disintegration of one or other of the parent substances, uranium or thorium A schematic representation of the successive products of the uranium and thorium families respectively is given in Tables XVII and XVIII.

In these Tables, a radio-element is always placed lower down in the table than its parent substance, when its production has involved the emission of an α-radiation ; in this case its atomic weight is always less by four units than that of the parent substance, and this is expressed in the left-hand column If the daughter element is the result of the emission of a β-radiation by the parent element, so that its atomic weight is practically unchanged, it is placed to the right alongside its parent element.

In certain cases two arrows branch off from the parent substance, indicating that this substance is transformed into two different new products This behaviour requires a special explanation. Thus both ionium and uranium Y are produced by the emission of α-rays from the parent uranium II (for details, see p. 175) , on the other hand, of the two products which succeed RaC, ThC and AcC respectively, one is produced by the emission of α-, and the other by the emission of β-radiation. Such a branching in the disintegration process is known as *dual decay* The " *branching ratio* " may be very different in different cases. Thus, from 10,000 RaC atoms, only three are transformed into RaC″, whereas 9997 go to form RaC′ ; the reverse holds in the case of AcC, where the majority of the atoms are transformed into AcC″ (about 9984 in 10,000) ; finally, with ThC the difference is less marked, for 65 % are transformed into ThC′, and 35 % into ThC″. About 3 % of the atoms of Uranium

TABLE XVII

Uranium-Radium* and Actinium Disintegration Series

Atomic Weight.

	Radium series	Actinium series
238	Uranium I	
234	Uranium X₁ → Uranium X₂ → Uranium II	
230	Ionium (? → Uranium Y → Protactinium)	
226	Radium	Actinium → Radioactinium
222	Ra Emanation	Actinium X
218	RaA	AcEm
214	RaB → RaC → RaC' (? RaC″)	AcA
210	RaC″ → RaD → RaE → RaF	AcB → AcC → AcC' (? → AcD); AcC″ → AcD
206	RaG	

* Further details about the uranium series (branching at UX₁) are given in Chapter XXIV on p. 175.

II (1) pass over into the actinium series, whereas the remainder traverse the path of the radium series.

TABLE XVIII

Thorium Disintegration Series

Atomic Weight.

232	Thorium
	↓
228	Mesothorium 1—→Mesothorium 2—→Radiothorium
	↓
224	Thorium X
	↓
220	Th Emanation
	↓
216	ThA
	↓
212	ThB--→ThC—→ThC′
	↓ ? ↓ ?
208	ThC″—→ThD

The observation of such small branchings as those of RaC″ and AcC′ suggests the possibility that there may be other places in the disintegration series, as yet unobserved, at which multiple decay may take place. Thus, it has been recently established by means of the extremely sensitive scintillation method, that $\frac{1}{11,000}$ of the atoms of ThC disintegrate with the emission of a-rays of range equal to 11·3 cm. (cf. p. 21 and Fig. 27) (2), and also in the uranium series a new branch product, uranium Z, has been discovered (3).

The following Table XIX shows (4) the relative activities of pitchblende and the disintegration products of long life contained in it. This Table also gives the number of ions produced by the a-rays sent out from each of these products, and the relative number of atoms disintegrating per second.

It will be noticed that the number of atoms disintegrating per second in the case of uranium is twice that for radium. This is

explained by the fact that uranium consists of the two radio-elements uranium I and uranium II in equilibrium with each other (see also p. 88 and p. 173). On the other hand, we notice that only one atom of protactinium disintegrates for every 30 of both uranium I and uranium II. Two possible explanations of this suggest themselves.

TABLE XIX

Substance.	Activity.	Number of Ions produced × 10^{-5}.	Relative Number of Atoms disintegrating per Second.
Pitchblende -	1573	1·59	7·82
Uranium - -	313·5	1·22	2·04
Ionium - -	173	1·37	1·00 *
Radium - -	192	1·45	1·05
Polonium - -	200	1·58	1·00
Protactinium -	5·1	1·41	0·029

Either only a fraction of uranium is transformed into protactinium, the major part taking the line of the ionium-radium series, or it may be that protactinium is not derived from either uranium I or uranium II, but from a third isotope of uranium associated with these (say of atomic weight 239) (5).

* Reference unit.

DETERMINATION OF VERY LONG AND VERY SHORT HALF-VALUE PERIODS. RELATION BETWEEN HALF-VALUE PERIOD AND VELOCITY OF THE RAYS EMITTED

THE half-value periods of the radio-elements vary between very wide limits, which range from intervals of time that are almost inconceivably small (e g for ThC', $T = 10^{-11}$ sec.), to periods that are literally enormous (e g for thorium, $T = 2\ 2 \ . \ 10^{10}$ years). Although the evaluation of these values cannot be performed directly, their determination can be made in a relatively simple manner by other means, and in many cases it is possible to determine them in several independent ways.

Suppose we consider the case of uranium I. If this element is in equilibrium with the later disintegration product radium, as is always the case in minerals of great geological age, then (p. 88) the product of the number of available atoms and the disintegration constant in the case of uranium I is equal to the corresponding product for radium,

$$U_I \ \lambda_{U_I} = Ra \ . \ \lambda_{Ra},$$

or if the amounts of the elements in grams be considered, whereby we must take account of the ratio of the atomic weights (238/226),

$$U_I \ . \ \lambda_{U_I} = \frac{238}{226} \ . \ Ra \ . \ \lambda_{Ra}.$$

Now the ratio of the radium and uranium contents of old minerals has been established by numerous chemical analyses to be $3\cdot3 \ . \ 10^{-7}$.[*] Since $\lambda_{Ra} = 1\cdot39 \ . \ 10^{-11}$ sec.$^{-1}$, it follows that

$$\lambda_{U_I} = 4\cdot85 \quad 10^{-18} \text{ sec.}^{-1},$$

and
$$T = 4\cdot51 \ . \ 10^9 \text{ years}.$$

Another method which leads to the evaluation of the required disintegration constant is the counting of the a-particles emitted

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[*] The value found for uranium also holds for uranium I, since the amount by weight of uranium II present in uranium is only 0 04 %

per second by a known quantity of uranium. Since it has been established that in disintegration each atom ejects only one α-particle (p. 20), it follows that the number of ejected α-particles (which can be counted) must be equal to the number of atoms disintegrating. Moreover, the disintegration constant is equal to the ratio of the number of atoms disintegrating per unit of time to the total number of atoms of a radio-element present (p. 82). Now 1 gm. ($=2 \cdot 55 \cdot 10^{21}$ atoms) of uranium emits $2 \cdot 3 \cdot 10^4$ α-particles per second, half of these being due to uranium I, and the other half to uranium II. From this we have

$$\lambda_{U_I} = \frac{1 \cdot 15 \cdot 10^4}{2 \cdot 55 \cdot 10^{21}} = 4 \cdot 5 \quad 10^{-18} \text{ sec.}^{-1},$$

and

$$T = 4 \cdot 77 \cdot 10^9 \text{ years}$$

This value is in good agreement with that found by the method previously discussed.

DETERMINATION OF VERY SHORT HALF-VALUE PERIODS RELATION BETWEEN DISINTEGRATION CONSTANT AND VELOCITY OF THE • RAYS

A simple relation has been found to exist between the disintegration constant and the range (or velocity, see p 25) in the case of radio-elements that emit α-rays. By virtue of this relation we are enabled by extrapolation to evaluate the disintegration constant even in the case of elements of extremely short life If, as in Fig. 32, we plot the logarithm of the range as abscissa, and the logarithm of the disintegration constant as ordinate, we obtain a straight line for each of the three disintegration series. The range corresponding to a definite disintegration constant is greater for the actinium series than for the thorium series, whilst that for the latter series is greater than the range for the uranium series *

Thus we obtain the value 10^{11} sec.$^{-1}$ for the disintegration constant of ThC′ from the known range 8·67 cm. at 15° C., by utilising Fig. 32. This corresponds to a half-value period of 10^{-11} seconds

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* Mathematically, we can express the relation in the form

$$\log \lambda = A + B \cdot \log R_0,$$

where R_0 is the range at 0° C., and A and B are constants, the values of which for the uranium-radium series amount to $-37 \cdot 7$ and $+53 \cdot 9$ respectively. Each disintegration series has a characteristic value of A, whereas the value of B is common to all three series (6). The relation does not hold for actinium X, which has an abnormally small range, as may be seen from Fig. 32.

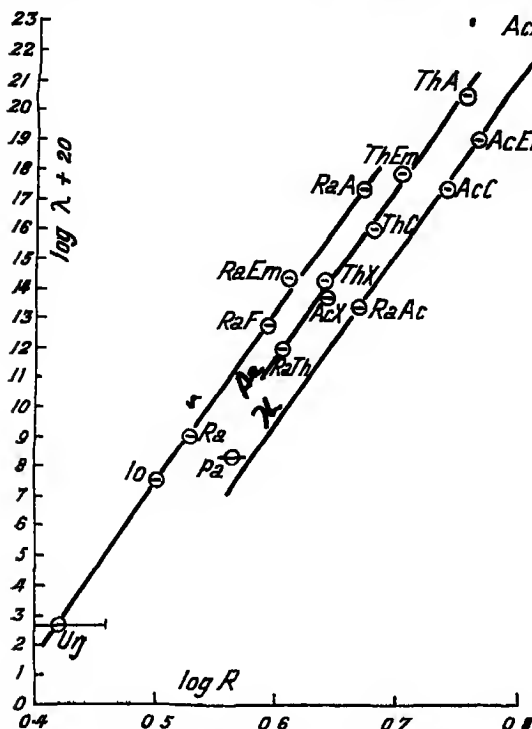A similar calculation gives the value ca. 0·1 sec. for the half-value period of thorium A. The direct determination of this quantity by means of a rapidly rotating disc with suitable electroscopic arrangement results in the value $T = 0·145$ sec. for ThA.

Fig 32 Relation between the Range and the Disintegration Constant for α Rays

With β-rays, too, a large velocity is indicative of a short life of the radio-element emitting them. But in this case, the investigation of the quantitative relation is rendered difficult by the complex nature of the β-radiation. As would be expected, this relation between disintegration constant and velocity is only valid for the primary β-rays emitted by the nucleus, and not for the secondary rays liberated from the extra-nuclear electron system. But the secondary rays generally preponderate in the β-ray spectrum (see p. 73), and the separation of the primary rays is fraught with difficulty. The following Table XX shows that the half-value period increases as the velocity of the particles diminishes (7).

TABLE XX

Relation between the Velocity and the Half-Value Period for β-Rayers.

Element.	Velocity of the Primary β-particles in per cent. of the Velocity of Light	Half-Value Period.
RaB	80·2	26·8 minutes.
ThB	73·9	10·6 hours.
RaD	40·2	16-20 years.

XII

CHEMICAL PROPERTIES OF THE RADIO-ELEMENTS. ISOTOPY

ONLY a few of the radioactive elements, *e.g.* thorium, uranium, and radium, can be obtained in weighable quantities. The determination of the properties of these elements is carried out by means of the usual chemical methods, for the radioactive nature of the element does not affect its chemical properties, and during the time of its stability an atom of radium, to take one example, is quite analogous to the atoms of the typical metals of the alkaline earths. From the moment of its disintegration, however, we are no longer dealing with an atom of radium, but with an atom of a new element—the emanation produced from radium—which, so long as it lasts, behaves entirely like the atoms of the other rare and inert gases.

The large majority of the radio-elements can only be obtained in unweighable quantities, and in many cases the amounts of them available are vanishingly small. The determination of the chemical properties of these elements is rendered possible by the application of two facts which are of fundamental importance in radiochemistry (a) It has been observed that the behaviour of the elements in extreme dilution is essentially the same as that shown at concentrations usually employed (See Chapter XIV for details.) (b) It has been established, and this involves a principle quite new to chemistry, that a chemical element can occur in different types, the chemical properties of which are identical, in spite of differences in atomic weight that are often considerable. Furthermore, many of the radioactive substances have been found to be none other than radioactive types of chemical elements that have been known for a long time. Such types of one and the same element are called *isotopes.*

Whereas some of the radio-elements can be separated and prepared in the pure state from minerals in which they occur together with numerous other elements or from preparations in which they have been mixed artificially with other elements, other radio-elements

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are met with which are completely inseparable from certain elements. It has been mentioned that it is possible to separate radium in the pure state from uranium minerals containing numerous other elements ; moreover, it is also possible to separate polonium, which is present in still smaller quantity, both from pitchblende and from any elements whatsoever, with which it has been mixed. On the other hand. RaD, which is always present in uranium minerals in much greater quantity, cannot be separated from the lead associated with these minerals In fact, when we apply the usual chemical methods, we cannot produce the slightest alteration in the original concentration ratio between RaD and lead. The same behaviour is shown by mixtures of mesothorium and radium, ionium and thorium, etc.

This chemical inseparability is of an entirely fundamental nature, as is proved by :

(1) The extensive experimental evidence adduced in favour of it ;

(2) The success which has resulted from including such inseparable substances in the same place in the periodic classification ;

(3) The consideration of isotopy in the light of the constitution of the atoms.

In this chapter we shall discuss only the *experimental evidence in favour of isotopy*, whereas Chapters XIII and XVI respectively will be devoted to the points (2) and (3).

If, for instance, we endeavour to separate or to concentrate the RaD-content from lead chloride obtained from pitchblende, we find that we have not advanced a step in this direction as a result of numerous crystallisations of known lead compounds (*1*), or by partial sublimation of these compounds or of the metallic lead. Other methods are equally fruitless, viz electrolysis in aqueous solution or in the fused state, adsorption by charcoal or other substances, diffusion, dialysis, and so on (cf. however, Chapter XIX). The difficult separability of closely related substances, like those of the rare earths, is a phenomenon well known in chemistry, but the difficulty of separation in such cases is not comparable with that involved when we are dealing with isotopes. We can always displace the concentration ratio in a mixture of the rare earths by means of various chemical operations, but this is not possible with isotopes

unless we have recourse to special methods (p. 141), even though the quantitative determination of the ratio of the constituents, especially in the case of the rare earths, is often faced with great difficulties, quite unknown in radiochemistry. For we can detect the RaD-content of a lead-RaD mixture in a most convenient and simple manner by means of an electroscope, using the α-radiation of its later disintegration product, polonium.

If we do not proceed from a natural mixture of RaD and lead such as is found in minerals, but prepare a mixture artificially by mixing a quite pure RaD salt, obtained from the decay of the gaseous emanation, with a lead salt, we find that this mixture likewise shows the behaviour described above

In consequence of the ease with which it can be detected, RaD is particularly suitable for the control of the concentration ratio of a mixture of lead isotopes before and after the application of chemical operations Nevertheless, in the investigation of the properties of an unmixed isotope—e g its spectral behaviour, the absolute solubility of its salts, its density, its normal electrochemical potential, etc., and especially its atomic weight—the stable end-product of the uranium series, RaG, is to be preferred, for although it is inactive, it is an isotope of lead that can be obtained in much greater quantities.

Pure RaG is obtained from uranium minerals that have not been contaminated by common lead in the course of geological time, for example, a crystalline uraninite from East Africa Owing to the smallness of the quantity of RaD that can be obtained from radium emanation, it is not possible to carry out an atomic weight determination of this isotope of lead, and our conclusions as to the difference of the atomic weights of RaD and common lead (atomic weight $= 207 \cdot 18$) are based solely on the formula

$$\underset{226}{\underset{\text{of Ra)}}{(\text{Atomic weight}}} - 4 \times \underset{16}{\underset{\text{of He)}}{(\text{Atomic weight}}} = \underset{210}{\underset{\text{of RaD)}}{(\text{Atomic weight}}}$$

But in the case of RaG it has been possible to establish experimentally that its atomic weight is different from that of common lead. The value $206 \cdot 05$ (2) was found for the atomic weight of RaG, whereas the value predicted by calculation was

$$\underset{226}{\underset{\text{of Ra)}}{(\text{Atomic weight}}} - 5 \times \underset{20}{\underset{\text{of He)}}{(\text{Atomic weight}}} = \underset{206}{\underset{\text{of RaG)}}{(\text{Atomic weight}}}$$

Most uranium minerals, *e.g.* pitchblende from Joachimstal, contain ordinary lead in addition to numerous other accessory elements, and under the most favourable conditions we obtain from this mineral a mixture of about 36 % of lead with 64 % of RaG, with a " combining weight " of 206·4 (*3*).   On the other hand, the mineral curite (containing 21 3 % PbO, and 74·2 % UO_3 (*4*)), which occurs in large quantity at Katanga (Belgian Congo), contains no trace of ordinary lead, and the lead extracted from it is pure Radium G (*5*).

The specific gravity of metallic RaG is related to that of common lead in the same ratio as their atomic weights, from which it follows that the atomic volumes of the two elements are equal (*6*).   This is shown in Table XXI.

<div align="center">TABLE XXI</div>

<div align="center">Atomic Volumes of Different Types of Lead</div>

Type of Lead.	Atomic Weight	Specific Gravity	Atomic Volume.
Ordinary Lead - -	207·20	11·337	18·28
Uranium-lead (RaG) -	206 09	11·273	18·28 ·

From the fact that the density of the saturated solution of RaG nitrate in water is correspondingly smaller than that of lead nitrate in water, it follows that their molar solubilities are equal (*7*) (see Table XXII).   Moreover, no difference has been detected in the refractive indices of the saturated solutions, as is also indicated in Table XXII

<div align="center">TABLE XXII</div>

<div align="center">Saturated Aqueous Solutions of the Different Types of Lead</div>

Salt	Molar Concentration	Refractive Index
Ordinary Lead Nitrate -	1·7993	1·7815
Uranium-lead Nitrate - -	1·7991	1·7814

The normal electrochemical potential of RaG in a solution of RaG-$(NO_3)_2$ is at least within $\frac{1}{10}$ milli-volt identical with that of lead in a solution of $Pb(NO_3)_2$.   The mobility of these two ions is identical within $\frac{1}{100}$ % (*8*).   Also the Röntgen spectra have been found to be identical to a degree of accuracy of about $\frac{1}{200}$ % of the wavelength (*9*), and, moreover, the optical spectrum reveals only

exceedingly small differences (p. 132) (*10*). The melting points do not differ by more than 0·06° C (*11*).

• The commencement of supra-conductivity for ordinary lead (7·2° A.) was found to be identical within $\frac{1}{40}$° with the temperature at which supra-conductivity begins with uranium-lead. Moreover, in the form of the resistance curves between 7·2° and 15° A. no difference could be detected (*12*). For two isotopic mixtures of mercury obtained artificially and differing in combining weight by 0·1 of a unit, the resistance was found to be the same to within $1 : 10^6$ (*13*).

Still another isotope of lead, ThD, the end-product of the thorium series, is obtainable in weighable quantities   It should possess an atomic weight of $232 - 6 \times 4 = 208$ (*14*). Unfortunately, the large majority of thorium minerals also contain uranium (sometimes also ordinary lead), and hence we obtain from these minerals a mixture of RaG with ThD, in consequence of which the atomic weight appears to be greatly reduced. The purest ThD hitherto obtained was separated from a thorite from Norway containing practically no uranium, and it yielded a combining weight of 207 9 (*15*).

From the rest of the isotopes, ionium is the only one that can be obtained in weighable quantities. It is isotopic with thorium. Io-Th mixtures prepared from pitchblende from Joachimstal, and having an ionium content of 30 %, possess a combining weight of 231·51, whereas thorium has an atomic weight of 232 12.

All the known isotopes (*16*) of radioactive elements are listed together in Table XXIII, which also includes the atomic weights and half-value periods of the substances concerned. The grouping of the elements was carried out in most cases on the basis of chemical experiments, *e g.* by establishing their inseparability from known substances. (In this connection, see also Chapter XIV.) In the case of the substances of shortest life, recourse had to be made to the radioactive " displacement law " (see the following Chapter). Each group is arranged in the order of diminishing half-value period, and begins with the member of longest life, from which, in general, it receives its name. Thus we speak of " types of lead," " types of thorium," and so on   We notice that the Table, in which the elements gold and mercury are included for purposes of completeness, embraces only the last two horizontal rows of the periodic classification (cf. Table XXV, p. 126, which presents the entire periodic system of the elements). The isotopes of mercury, and of other non-radioactive substances, are referred to on p. 137.

TABLE

Radioactive Isotopes (with Atomic

Period	Group I	Group II.	Group III	Group IV
VI.	Au 197 2 stable	Hg 200 6 stable	Tl 204 4 stable AcC″ 206 4 76 minutes ThC″ 208 3 2 minutes RaC″ 210 1 32 minutes	Pb 207 18 stable RaG 206 stable ThD 208 stable AcD 206 stable (?) RaD 210 16 years ThB 212 10 6 hours AcB 210 36 1 minutes RaB 214 26 8 minutes
VII		Ra 226 0 1580 years MsTh 1 228 6 7 years AcX 222 11 2 days ThX 224 3 64 days	Ac 226 20 years MsTh 2 228 6 2 hours	Th 232 1 2 2 . 10^{10} years Io 230 10^5 years RdTh 228 1 90 years UX_1 234 23 8 days RdAc 226 18 9 days UY 230 25 5 hours

XXIII

Weights and Half-Value Periods)

Group V	Group VI	Group VII.	Group VIII (0).
Bı　　　209 0 　stable RaE　　　210 　4 85 days ThC　　　212 　60 8 minutes RaC　　　214 　19 5 minutes AcC　　　210 　2 16 minutes	Po　　　210 　136 days RaA　　　218 　3 05 minutes ThA　　　216 　0 14 seconds AcA　　　214 　0 002 seconds AcC′　　210 　10^{-3} seconds RaC′　　214 　10^{-7} seconds ThC′　　212 　10^{-11} seconds		RaEm　　222 　3 810 days ThEm　　220 　54 5 seconds AcEm　　218 　3 9 seconds
Pa　　　230 　ca　10^4 years UX₂　　234 　1 15 minutes UZ　　　234 　6 7 hours	U I　　　238 2 　4 5 . 10^9 years U II　　234 　2　10^6 years		

XIII

ISOTOPY AND THE PERIODIC CLASSIFICATION. ALTERATION OF CHEMICAL CHARACTER WITHIN A TRANSFORMATION SERIES. THE DISPLACEMENT LAWS

THE discovery of the large number of about forty radioactive substances brought chemists face to face with the problem as to how these substances were to be accommodated in the natural system of the elements. A method for the rational grouping of the elements suggests itself when we take the phenomenon of isotopy as the basis of our considerations, as may be seen from Table XXIII. Most of the radio-elements are chemically inseparable from other radioactive elements or from stable elements If we adhere to the principle of assigning isotopes to one and the same place in the periódic classification, it is found that from uranium to thallium the number of available places in the classification suffices for the accommodation of all the radio-elements. In so doing, we implicitly alter the original basis of the periodic classification, for we can no longer regard the atomic weight as fundamental for the place occupied by an element in the natural system of the elements, since the atomic weights of many isotopes differ

A particularly important relation is revealed when we apply this method of grouping the radio-elements to obtain the solution of the question as to what changes in the chemical nature of the elements ensue from the emission of an a- or a β-particle. In other words, how does the chemical nature of the radio-elements change as we pass from one element to another in a transformation series ? The required relation is immediately recognised when we compare Tables XVII and XVIII, which give the sequence of and type of radiation emitted by the radio-elements, with Table XXIII, which indicates the positions of the radio-elements in the periodic classification. In this way we obtain the following " *displacement law.*"

The emission of a-particles by an element results in the production of an element situated two places lower down in the natural sequence

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of the elements, whereas when the disintegrating element emits β-rays, an element is produced which is situated one place higher in the system. In this connection we regard the whole of the chemical elements as being arranged in a continuous series, in somewhat the same manner as they were represented by Lothar Meyer in his atomic volume curve. In Mendeléeff's table we must remember that the individual periods are only portions of this continuous series, and that consequently a transition of an element in the zero group to a place situated two places lower down in the series involves the appearance of an element in the sixth group of the preceding horizontal row. If this is clear, Table XXIV will be immediately intelligible. It represents the uranium-radium series, and shows the arrangement of the elements in the last two horizontal rows of the periodic classification   The branching of the actinium series is not included, as its origin is still somewhat obscure   In this Table, an arrow directed towards the left, and always embracing two groups, indicates the emission of an α-particle, whereas an arrow directed to the right, and reaching only the next group, represents the ejection of a β-particle   Corresponding to the diminution in atomic weight, the arrows representing α-transformations are inclined to the horizontal. In particular, we notice that in the case of RaC, which suffers " dual disintegration " (see p. 100), the displacement law applies both to the product resulting from the emission of an α-particle and for that attendant upon a β-disintegration , i e. RaC″ is situated two places lower and RaC′ one place higher than RaC. By means of an analogous schematic representation, the validity of the displacement law can also be shown for the actinium and for the thorium series; in fact this can be directly seen by a comparison of Tables XVII and XVIII respectively with Table XXIII *

From the displacement law it follows that, when an α-transformation is succeeded by two β-transformations in one and the same disintegration series, an isotope must always be the result, as in the transition of U_I *via* UX_1 and UX_2 into U_{II}, which is isotopic with U_I. Two isotopes that are genetically related in this way must necessarily exhibit a difference in atomic weight of four units ($=$one α-particle), and from this example we see clearly that the atomic

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* Conversely, it has been mentioned in the preceding pages that for the radio-elements of shortest life, the recognition of their chemical nature and their consequent inclusion in the table of isotopes were only rendered possible by the assumption of the validity of the displacement law.

TABLE XXIV

Arrangement of the Uranium-Radium Series in the Periodic Classification

	Atomic Weight	Group I	Group II	Group III.	Group IV.	Group V	Group VI	Group VII	Group VIII. (0).
Period VI.	206				RaG				
	210				RaC″ → RaD → RaE → RaF				
	214				RaB → RaC → RaC′				
	218						RaA		
	222								RaEm
Period VII.	226		Ra						
	230				Io				
	234				UX₁ → UXₐ → U II				
	238					U I			

weight cannot be of fundamental importance in deciding the position of an element in the periodic classification. The positional number of an element, *i.e* its *ordinal* or *atomic number*, must depend on some other quantity, and we shall have to speak of this in Chapter XVI.

XIV

THE CHEMICAL BEHAVIOUR OF EXTREMELY SMALL QUANTITIES OF A SUBSTANCE

FROM the genetic relation existing between the radio-elements it follows that we can obtain only extremely small quantities of any radio-elements of short life (see radioactive equilibrium, p. 88). Thus if we possess a quantity of radium as large as 1 gram, we can under the most favourable circumstances obtain about 10 mg. of the relatively long-lived RaD from it, whereas we can obtain only 0·22 mg. of polonium, and as little as 10^{-14} mg. of the very short-lived RaC'. For this reason, the chemistry of the short-lived radio-elements is a chemistry of substances available in extremely small quantities, and therein lies its particular uniqueness, rather than in the radioactive properties, which do not influence the chemical behaviour (see p 107). From amongst the reactions particularly characteristic of every chemical element, those of a spectral or optical nature are inapplicable, for their sensitiveness is insufficient. We are restricted to the determination of the solubility of the elements and of their compounds, or to that of their electro-chemical behaviour and the like, whereby the usual methods of chemistry always have to be supplemented by electroscopic measure-ments (see p 9)

1. THE SOLUBILITY AND VELOCITY OF SOLUTION OF EXTREMELY SMALL QUANTITIES

Owing to the smallness of the amounts available, we cannot prepare a saturated solution of the short-lived radio-elements, and hence the direct determination of the solubility is not possible. But we can determine the relative velocity of solution. Thus if we immerse the surface, say a piece of gold sheet, on which we have collected the active deposit of radium, into a dilute solution of an acid for only a few minutes, we find that a greater fraction of the atoms of RaB than of RaC have gone into solution, whereas the fraction of RaA atoms dissolved is still smaller. The electrochemical nature of these substances thus diminishes down the series

RaA→RaC→RaB, corresponding to the chemical behaviour we should expect for the elements Po→Bi→Pb.

In individual cases we can also infer the existence of certain compounds of the radio-elements concerned, from the velocity of solution. For example, from the much smaller velocity of solution of the ThB deposited on the anode, as compared with that on the cathode, we can infer the existence of a ThB-peroxide of difficult solubility on the anode   This conclusion is confirmed by the observation that this difference in the velocities of solution can be annulled by the addition of a reducing agent to the acid used as solvent.

2. THE ELECTROLYTIC DEPOSITION OF SMALL QUANTITIES

The converse process to the solution of a metal is to be found in its electrolytic deposition. Thus if we electrolyse a solution of the active deposit of radium, RaA is deposited most readily, and RaB only with difficulty. If we perform the electrolysis with a small current. i e. if we do not exceed a certain cathode potential, it is possible to separate electrolytically the most noble of the available radio-elements in a very pure state. Particularly in the preparation of polonium, this method is of great importance. It can be prepared in this manner from solutions of the salts of radio-lead, which, in addition to Po, contains an isotope of bismuth (RaE) and three isotopes of lead (RaD, RaG, Pb)   Further details are given on p 166. Instead of by electrolysis, the separation of the radio-elements can also be effected by dipping a less noble metal into the solution of the radio-element concerned ; this is analogous to the deposition of copper from a solution of a copper salt on a small sheet of zinc   In radioactive investigations we very often require a preparation of RaC free from RaB   This can be obtained by dipping a small sheet of nickel into an acid solution of the active deposit of radium which no longer contains the short-lived radio-element RaA.

Both the methods described lead to the establishment of a potential series of the radio-elements, the most noble member of which is polonium, and the least noble radium.

3. DETERMINATION OF THE SOLUBILITY OF THE SALTS OF RADIO-ELEMENTS BY MEANS OF THE METHOD OF ADSORPTION AND PRECIPITATION

The chemical behaviour of an element is characterised primarily by the solubility of its different compounds. In order to gain

information as to the chemical nature of the radio-elements it was therefore necessary to establish the solubility relations of their compounds. In the case of the short-lived elements, which are present only in quantities too small to be weighed, this was not possible by the study of their pure salts, but only by adsorption and co-precipitation methods, in combination with theoretical considerations.

The Method of Adsorption

If we shake up a salt of low solubility, e.g. $BaSO_4$, with an aqueous solution of a salt the sulphate of which is readily soluble, e.g. bismuth sulphate, we find that an interchange takes place between the Ba-ions situated at the surface of the solid salt and the Bi-ions of the solution. Now the forces that strive to bind Bi- and SO_4-ions together to form a solid salt are much smaller than those operative in binding together Ba- and SO_4-ions This follows from the much greater solubility of bismuth sulphate in dilute acids * When the Bi-ions collide with the adsorbent, they will only rarely be held by the SO_4-groups, and hence the adsorption will be small The behaviour will be different, however, when the solution contains a salt such as $RaCl_2$, the cation of which forms with SO_4 a compound of low solubility. In this case the interchange between the Ra- and Ba-ions at the crystal surface will be a very active one, and the radium will be bound by the surface of the $BaSO_4$, i e it will be adsorbed. We can express this generally by saying .

A cation will be adsorbed by a difficultly soluble salt when it forms with the anion of the adsorbing salt a compound, the solubility of which in the solvent is small The less the solubility of the compound involved and that of the adsorbent, the stronger will be the adsorption

By means of this method it can be readily proved, for instance, that ThX and AcX (both types of Ra) form sulphates of very low solubility, whereas the " B "-products (types of lead) give rise to sulphates of fairly low solubility, on the other hand, the sulphates of the " C "-products (types of Bi) and also of polonium, are easily soluble If we carry out these experiments in potassium hydrate, in which we know the solubility of lead sulphate to be greater than that of bismuth sulphate, we find a correspondingly weaker adsorption of the B-products than of the C-products

* More accurately expressed, it is not solely a question of the magnitude of the forces holding the ions together in the crystal lattice, but of the excess of these forces over those which seek to bind the ions to molecules of water, or to hydrate the ions.

The Method of Precipitation

Instead of establishing which salt of low solubility adsorbs the radio-element concerned, we may also proceed along the following closely allied path. We add a soluble barium salt to the solution of the radio-element, say the active deposit of thorium, and precipitate it as sulphate. Whereas the ThB is also precipitated, the ThC remains in solution, from which we may likewise conclude that the first compound (lead sulphate) is only soluble with difficulty, whilst the latter compound (bismuth sulphate) is readily soluble. *A radio-element will always be precipitated in a higher degree along with a deposit of low solubility, the less soluble is its compound with the negative constituent (anion) of the precipitate.*

From the results of experiments on adsorption and precipitation we may also conclude, in particular, that for the extremely small quantities involved in the case of the radio-elements, the fundamental condition for their assimilation in the precipitate is primarily their difficult solubility, and not, as one might be inclined to conclude from experiments with weighable quantities, the existence of isomorphism   .

4 VOLATILITY OF EXTREMELY SMALL QUANTITIES

The observation of the proportion in which the different components of the active deposit volatilise when heated for a short time at high temperature, enables us to form a conclusion as to the sequence of the boiling points of the radio-elements concerned, or of their compounds. Thus in air at 700° C. none of the " C "-products volatilise, whereas the " B "-products are already appreciably volatile; from this it follows that ThB- is more volatile (*1*) than ThC-oxide (*i.e.* lead and bismuth oxides respectively). This method can also be applied for the partial separation of short-lived radio-elements.

Nevertheless, an accurate determination of the boiling point of extremely small quantities is not possible, chiefly owing to the preponderance of the process of sublimation. In this respect, the behaviour of the emanations is very instructive. Thus a quantity of radium emanation of the order of magnitude of 1 Curie = 0·6 mm.³ manifests a sharply defined boiling point at − 62° C. and a freezing point at − 71° C., but quantities of emanation of the order of magnitude of 10^{-7} Curie no longer possess a definite boiling point. Such small quantities already begin to sublime appreciably at − 164° C., and at − 125° C. practically no condensation can be recognised.

5. Velocity of Diffusion.   Determination of the Valency and the Degree of Dispersion.   Colloidal Radio-elements

The determination of the velocity of diffusion in water of the ions of all the radio-elements with a half-value period not very much less than one hour can be performed by the usual method. Here the extremely small concentration is, in fact, of particular advantage, seeing that we have to operate with solutions as dilute as possible.

We can likewise determine with little difficulty the velocity with which the radioactive ions move in an electric field, i.e. their so-called electrolytic mobility. The ratio of this to the velocity of diffusion immediately reveals to us the charge carried by the ion concerned, and hence its valency. Since the mobilities of the majority of inorganic ions differ amongst themselves only by a few per cent., we can also evaluate the valency, which can only amount to a small integral number (1 to 4), directly from the velocity of diffusion. From the constants of diffusion 0 33, 0·46, and 0 66 cm.^{2} day^{-1} for radioactinium (thorium isotope), actinium (homologue of lanthanum), and actinium X (isotope of radium) respectively, we can, for instance, calculate that the respective valencies are 4, 3 and 2.

Diffusion experiments further show that under certain circumstances radio-elements can exist in the colloid form. Thus in neutral and in weakly acid solution, polonium is partially colloidal ; it diffuses slowly does not dialyse through a parchment membrane, etc. This behaviour serves as the basis of a method of concentrating the polonium in radio-lead ; the polonium remains behind in the dialyser, and the crystalloidal lead diffuses outwards.

Isotopes of bismuth, too, show such an extensive tendency to appear in colloidal form that, for example, when we filter a neutral or weakly acid solution of ThB + ThC, the latter (type of bismuth) is for the most part retained by the filter.

A particularly striking confirmation of the colloidal nature of the solution of some of the radio-elements has been furnished by the following observation. When ions or other colloids were added to the solutions, the phenomena of the inversion of charge and precipitation characteristic of colloids were obtained in exactly the manner to be expected in such cases (2).

The molecular weight of the emanations can be approximately determined by the observation of the velocity with which they flow through small orifices. In this way we obtain for actinium emanation values lying between 222 and 218.

XV

APPLICATION OF THE RADIO-ELEMENTS AS INDICATORS IN PHYSICAL AND CHEMICAL INVESTIGATIONS

As we have seen, many difficulties had to be overcome before the chemical nature of the radio-elements could be recognised. But now that we know the nature of all of them with great certainty, we can apply them, conversely, to obtain information on the behaviour of known substances in such small concentrations that they are not amenable to a normal investigation. Those elements, such as lead and bismuth, which exist both in the form of a stable type and as radioactive isotopes, are particularly suitable for investigations of this kind. In these cases we can bridge over the whole region from quantities that can only be detected by radioactive means to those that can be weighed, by mixing the stable type with a radioactive type of element in varying proportions. In this manner we are able to investigate completely the behaviour of one and the same chemical element over a very wide range. In problems of this kind, where the radio-element is not the object but the agent of the investigation, we say that the radio-elements serve as "indicators" (3)

Suppose we wish to find the solubility of lead chromate, which is almost insoluble. A very suitable method for dealing with this problem is to mix a known quantity of a lead salt with a quantity of ThB, the strength of which is known in relative electroscopic units. Owing to the inseparability of these isotopes, we can be certain that the ratio of ThB to lead will remain the same, no matter what chemical operation we may perform. Thus if we precipitate the lead as chromate, filter, and prepare a saturated solution of this lead chromate by shaking up with water, we shall be able to establish in a quick and convenient manner the extremely small fraction of the chromate present in the solution by measurements with an electroscope, whereas we could not determine it by weighing. The results would supply us with the solubility of lead chromate.

An interchange of the atoms and molecules within a homogeneous substance can be readily followed by means of radioactive indicators. The simplest example of such a kinetic problem is presented by the addition of an activated $Pb(NO_3)_2$ solution to an inactive solution of $PbCl_2$ of equivalent strength. By crystallising from this mixture a sample of lead chloride, we can determine whether it only contains those lead atoms that were combined with chlorine before the mixing, or whether it also contains lead atoms which were originally combined in the form of nitrate. As we should expect, the result of such a determination demonstrates that the lead atoms of the lead chloride were derived in equal quantities from the two initial solutions. On the other hand, if, say, activated lead nitrate and inactive tetraphenyl-lead, or another compound in which the lead atom is linked with carbon in a non-ionisable form, be simultaneously dissolved and then separated by crystallisation, we are unable to detect any interchange of the lead atoms between the lead nitrate and the organic compound of lead (4).

The interchange between the solid and liquid phases, as between metal and ion, or between a salt and its saturated solution, is more difficult to picture, and for this reason more important to investigate than the positional interchange in solutions. These processes can be readily traced in their dependence on time by means of radioactive types of lead and bismuth, and the observed behaviour can be made the basis of a method of measuring the absolute surface of powders, which is of importance in many experiments on adsorption (5). Even when we are only dealing with the relative comparison of surfaces, radio-elements can be applied with advantage (6). By means of radioactive indicators, we can study the simple, and, from the theoretical view-point, the very important case, which Maxwell termed " self-diffusion," and which he frequently carried out in the form of a mental experiment. We only need to measure the velocity of diffusion of molten or solid active lead in inactive molten or solid lead, in order to obtain the constant of self-diffusion of lead.

From an electrochemical point of view it is of interest to investigate the deposition potential of an ion in the case in which the amounts separated out are insufficient to coat the electrode with a continuous layer, even of only atomic thickness. For example, by the application of the active type of bismuth, RaE, it is possible to determine the deposition potential of bismuth even in this region, which would otherwise be inaccessible.

Occasionally we can also solve problems in preparative chemistry by having recourse to radio-elements. Thus the existence of the long-sought-for gaseous hydrides of bismuth and lead was first proved by the aid of the radioactive type of bismuth (ThC) and the type of lead (ThB) (8). Naturally, there are also many problems in analytical chemistry which can often be simply and elegantly solved with the assistance of radio-elements, particularly those involving small quantities, such as co-precipitation in the formation of precipitates, the washing of precipitates and experimental vessels, etc. In fact, it is sometimes advantageous to use a radio-element as an indicator for the chemical reactions of another isotopic radio-element that emits radiation of lesser intensity. Thus the most suitable methods of separation for actinium can be studied by using $MsTh_2$, and those of Pa by using UX_2 (9). Lead that has been activated by the addition of a radioactive isotope can further be used to study, say, the circulation of this element in the animal or plant organism (10)

Technical investigations can also benefit from the application of radioactive indicators It has been found possible to determine quantitatively, and with speed and accuracy, the different permeability to air of almost completely air-tight gummed materials (such as those used for gas-masks), by using air containing traces of radium emanation (3) Moreover, by the use of polonium deposited electrolytically on the metals concerned, it has also been found possible to determine the degree of "spluttering" of metals bombarded by α-particles (7).

XVI

ISOTOPY AND THE DISPLACEMENT LAWS IN THE LIGHT OF ATOMIC CONSTITUTION. THE CURRENT REPRESENTATION OF THE PERIODIC CLASSIFICATION

WE have already described (see p. 62) the modern view of the constitution of atoms, which has rendered great service in the interpretation of the production of the radioactive rays and of series spectra. On this view we can also gain a deeper understanding of the nature of the above-mentioned chemical consequences of atomic disintegration. We assume that the material part of the atom is positively charged and confined to an exceedingly small space at the centre of the atom, whereas the entire remaining space within the atom is available for the revolving electrons * On the basis of this theory, since an α-particle carries with it two positive charges, an α-transformation entails a diminution of the nuclear charge number by two units, whilst a β-transformation involves an increase of this quantity by unity, since the loss of one negative charge must increase the excess of positive over negative carriers of charge in the nucleus by unity. The successive loss of one α- and two β-particles will thus lead us back to the original nuclear charge number. But according to the nuclear theory of the atom, identical nuclear charge number corresponds to the same number and arrangement of the electrons in the extra-nuclear system, and hence to identity in the chemical and spectroscopic properties. Thus we may regard the nature of isotopy as lying in the equality of the nuclear charge numbers, when the number—or at least the arrangement—of the constituent bricks of the nucleus is different.

* The radius of an atom has the approximate magnitude of 10^{-8} cm., that of the electron 10^{-13} cm., and that of the positive hydrogen nucleus 10^{-16} cm.; accordingly, the nucleus of the hydrogen atom is the particle which has the smallest dimensions known in physical science. It is called a *proton*, and we have evidence that it forms a primordial brick in the nucleus of more complex atoms (see p. 148).

TABLE XXV

Periodic System of the Chemical Elements.   (Short-period Representation)

Period	Group I a	b	Group II a	b	Group III a	b	Group IV a	b	Group V a	b	Group VI a	b	Group VII a	b	VIII Group			O
I													1 H 1 008					2 He 4·00
II		3 Li 6 94		4 Be 9 02		5 B 10 82		6 C 12 00		7 N 14 008		8 O 16 000		9 F 19 00				10 Ne 20·2
III		11 Na 23 00		12 Mg 24 32		13 Al 27 1		14 Si 28 3		15 P 31 04		16 S 32 07		17 Cl 35 46				18 Ar 39·88
IV.	19 K 39 10		20 Ca 40 07		21 Sc 45 10		22 Ti 48 1		23 V 51 0		24 Cr 52 0		25 Mn 54 93		26 Fe 55 85	27 Co 58 97	28 Ni 58 68	
		29 Cu 63 57		30 Zn 65 37		31 Ga 69 9		32 Ge 72 5		33 As 74 96		34 Se 79 2		35 Br 79 92				36 Kr 82·9
V.	37 Rb 85 5		38 Sr 87 6		39 Y 88 7		40 Zr 91 3		41 Nb 93 5		42 Mo 96 0		43 Ma		44 Ru 101 7	45 Rh 102 9	46 Pd 106 7	
		47 Ag 107 88		48 Cd 112 4		49 In 114 8		50 Sn 118·7		51 Sb 121·8		52 Te 127 5		53 I 126 92				54 X 130·2
VI.	55 Cs 132 8		56 Ba 137·4		57 to 71 Rare earths*		72 Hf 178 6		73 Ta 181 5		74 W 184 0		75 Re		76 Os 190 9	77 Ir 193·1	78 Pt 195 2	
		79 Au 197 2		80 Hg 200 6		81 Tl 204 4		82 Pb 207 2		83 Bi 209 0		84 Po 210		85 —				86 Em 222
VII.	87 —		88 Ra 226 0		89 Ac		90 Th 232 1		91 Pa		92 U 238 2							

* Rare Earths

VI. 57-71	57 La 139 0	58 Ce 140·2	59 Pr 140·9	60 Nd 144 3	61 —	62 Sm 150 4	63 Eu 152 0	64 Gd 157 3	65 Tb 159 2	66 Dy 162·5	67 Ho 163·5	68 Er 167·7	69 Tu 169 4	70 Yb 173 5	71 Cp 175·0

TABLE XXVI

Periodic System of the Chemical Elements. (Long-period Representation.)

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
I																	1 H 1 008	2 He 4·00
II.	3 Li 6 94	4 Be 9 02											5 B 10 82	6 C 12 00	7 N 14 008	8 O 16 000	9 F 19 00	10 Ne 20·2
III	11 Na 23 00	12 Mg 24 32											13 Al 27 1	14 Si 28 3	15 P 31 04	16 S 32 07	17 Cl 35 46	18 Ar 39 88
IV	19 K 39 10	20 Ca 40 07	21 Sc 45 10	22 Ti 48 1	23 V 51 0	24 Cr 52 0	25 Mn 54 93	26 Fe 55 85	27 Co 58 97	28 Ni 58 68	29 Cu 63 57	30 Zn 65 37	31 Ga 69 9	32 Ge 72 5	33 As 74 96	34 Se 79 2	35 Br 79 92	36 Kr 82·9
V.	37 Rb 85 5	38 Sr 87 6	39 Y 88 7	40 Zr 91 3	41 Nb 93 5	42 Mo 96 0	43 Ma —	44 Ru 101 7	45 Rh 102 9	46 Pd 106 7	47 Ag 107 88	48 Cd 112 4	49 In 114 8	50 Sn 118 7	51 Sb 121 8	52 Te 127 5	53 I 126·92	54 X 130·2
VI.	55 Cs 132 8	56 Ba 137 4	57-71 Rare* Earths	72 Hf 178 6	73 Ta 181 5	74 W 184 0	75 Re —	76 Os 190 9	77 Ir 193 1	78 Pt 195 2	79 Au 197 2	80 Hg 200 6	81 Tl 204 4	82 Pb 207 2	83 Bi 209 0	84 Po 210	85 —	86 Em 222
VII	87 —	88 Ra 226 0	89 Ac	90 Th 232 1	91 Pa	92 U 238 2												

Group

* Rare Earths

VI. 57-71															
57 La 139 0	58 Ce 140 2	59 Pr 140 9	60 Nd 144·3	61 —	62 Sm 150 4	63 Eu 152 0	64 Gd 157 3	65 Tb 159 2	66 Dy 162·5	67 Ho 163 5	68 Er 167 7	69 Tu 169 4	70 Yb 173 5	71 Cp 175·0

In Chapter XIII it was emphasised (p. 114) that the atomic number of the elements likewise decreases by 2 after an α-transformation, and increases by 1 for a β-transformation. This suggests the equality of the atomic number and the nuclear charge number. Such a conclusion is definitely proved by the investigation of Röntgen spectra and of the deflection of the α-rays. It was possible by these means to evaluate experimentally the magnitude of the nuclear charge number of most of the elements, and this was found to be identical with the positional number of the element concerned, *i.e.* with the atomic number. On p. 55 we stated the formula that enables us to decide upon the ordinal or atomic number of the element concerned when we know the frequency of a Röntgen spectral line, and on p. 28 we referred to the experiments on the deflection of α-particles.

Briefly stated, the investigations mentioned led to the following important results :

(1) The nuclear charge number of an atom is equal to the atomic number of the corresponding element. Moreover, this holds also in those three cases (argon-potassium, tellurium-iodine, cobalt-nickel), for which, on the basis of their chemical behaviour, the atomic numbers of the elements have long been known to stand in contradiction to the sequence of their atomic weights

(2) The nuclear charge numbers, and hence also the atomic numbers of isotopes such as RaG and Pb, are equal.

(3) In the interval between hydrogen (1) and uranium (92), we are familiar with carriers of all the 92 nuclear charge numbers, with the exception of three. The missing elements have the atomic numbers :

61. Rare Earth ;   85. Eka-Iodine ;   87. Eka-caesium *

These are the only chemical elements still unknown. Thus whereas there is possibly still a large number of isotopes that have not been discovered, the detection of new elements, with the exception of the three mentioned above, is not to be expected, unless we assume that there are elements with a still higher nuclear charge number than that of uranium. The investigations hitherto described thus lead us to the important result that we are able quite definitely

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* Until recently, the elements eka-manganese (43) and dvi-manganese (75) were unknown. Their existence in the earth has now been established by Röntgenographic means (*1*). Element 43 has been named *Masurium* (Ma), and element 75 *Rhenium* (Re).

to limit the expectations of chemistry, which had to proceed essentially in an inductive manner in its search for new elements, even after the formulation of the periodic classification.

From Röntgen spectra we can, in the first place, only decide on the atomic number of the missing elements. In this connection we may compare Fig. 16 (p 56), from which we at once recognise that the regularity of the straight lines would be immediately interrupted if, in the three positions mentioned of the abscissa, we were not to leave gaps for the three unknown elements, but insert the values of the ordinates for the next known element. On the other hand, we cannot gain information directly from the atomic number about the chemical nature of an element, because from amongst the four " atomic analogues " of Mendeléeff a knowledge of the atomic number only informs us as to the " horizontal neighbours," but not as to the " group neighbours " of the element, and these are still more important for the prediction of chemical properties. But since the position in the periodic classification is fixed by the atomic number, we can also recognise the chemical nature of the missing elements by utilising this classification. This we have done above, by making use of the terminology (eka-, dvi-) introduced by Mendeléeff Tables XXV and XXVI represent the forms assumed by the periodic system, when it is modified to take account of recent results We have introduced both a " short-period " and a " long-period " mode of representation of the classification, because for certain purposes each presents advantages (2).

Table XXIII (p 112) supplies information as to the different types in which the elements of the last two horizontal rows of the system, beginning with thallium, occur. The isotopes of the non-radioactive elements are indicated in Table XXVII (p 137)

XVII

ELECTRONIC AND NUCLEAR PROPERTIES OF THE ATOM

In the modern theory of the atom, a distinction is drawn between the nucleus and the electrons. This brings us face to face with the question as to which physical and chemical properties are primarily determined by the nucleus and by the electrons respectively. As already mentioned (p. 64), the emission of spectral lines is brought about by the return of electrons into their original orbit, after they have been removed from their normal orbit to a distance by the action of an external agency, such as the absorption of radiation, electron collision, etc. In the chemical reactions of the atoms, also, it is the electrons situated in the electron groups, particularly the outer ones, that are involved. Thus in the simplest case of ionisation, positive ions are formed when electrons leave the atom, and negative ones when the atom embraces additional electrons. It can be readily seen, by means of a simple consideration, that the gravitational forces within the atom are negligible as compared with those of an electrostatic nature. For example, the electrostatic attraction between the electron and the nucleus in the hydrogen atom is 10^{41} times greater than the gravitational attraction. The extensive independence of the chemical and spectroscopic properties of the atom, previously discussed, on the mass of the atom, and their exceeding similarity in the case of isotopes, follows directly from the theory of the atom. They are called *electronic properties* because of their dependence on the number and arrangement of the electrons in the extra-nuclear system.

Attempts have also been made to arrive at more definite ideas as to the manner in which atoms take up and part with electrons in the formation of ions, and more generally in chemical reactions. A very plausible assumption is that in the case of a non-reactive rare gas the outermost electron group possesses just that number of electrons which is necessary to "saturate" the group, so that there is no tendency for the atom to take up or to part with electrons. From

this assumption we can draw conclusions about the two elements adjacent to a rare gas, for their nuclear charge numbers differ from it by unity. In the electrically neutral state one of these will have in its outermost group one electron less than corresponds to " satura- tion," as in the case of the halogens The other will possess an excess electron in its completed group, as in the case of the alkalies. From this we can immediately deduce that they will tend to be transformed into a mono-valent negative and positive ion respec- tively, by taking up or by parting with one electron. In point of fact, we find quite generally that the strongest electro-negative elements immediately precede the rare gases in the periodic system, and that the strongest electro-positive elements immediately follow them On these lines we can attribute the chemical combination of, say, sodium and fluorine atoms to purely electrostatic forces. Each sodium atom hands over an electron to a fluorine atom, so that each type of atom in this way attains to the electron con- figuration of the inert gas neon, with the result that they become bound together electrostatically by virtue of the acquired opposite charges. We are reminded of the fact that sodium and fluorine ions, unlike their respective atoms, do not decompose water, and that this inertia of these ions towards reactions has hitherto been unintelligible to the chemist.

In chemical reactions it thus appears that only the outside electrons of an atom play a part, whereas in the excitation of charac- teristic Röntgen rays (see p. 75) the innermost electrons also are involved But in all these processes, the nucleus is not in the least influenced , and as long as it remains intact, the nature of the element is not altered, since changes in the electron configuration are always reversible. In this we have an explanation of the fundamental law of chemistry, according to which chemical elements can be neither produced nor destroyed Radioactive transforma- tions, however, alter the nucleus—for the ejected α- and β-particles are constituents of the nucleus—and we perceive a corresponding transmutation of elements in operation as a consequence of radio- active processes We are only able to call forth this transformation artificially when we make an effective attack on the nucleus. In recent years, such experiments have actually met with success (see p. 147).

Apart from radioactive processes, the mass of an atom is also for the most part seated in the atomic nucleus. Thus, together with the radioactive properties, the atomic weight is also a *nuclear property*.

THE TRANSITION FROM NUCLEAR TO ELECTRONIC PROPERTIES.

The differentiation between electronic and nuclear properties·
on the lines just indicated is of the greatest importance from the
practical point of view.   Of this we have already considered con-·
vincing examples ; but it cannot always be carried out with pre-
cision   Thus we have in the first place considered series spectra as
being an electronic property , but the wavelength of spectral lines
must also depend in a very small degree on the mass of the atomic
nucleus, for in consequence of the different structures of the nuclei
of isotopes (see p 125) the stray electrical fields emanating from the
nuclei must also be somewhat different, in spite of the equality of
the nuclear charge numbers   It has been established by means of
particularly delicate measurements that the wavelength of the
spectral line $405.8\mu\mu$ is $0\,0005\mu\mu$ larger for uranium-lead, and
$0\,00022\mu\mu$ smaller for thorium-lead than it is for ordinary lead (*1*).
Thus a difference in atomic weight of 1 % corresponds to a difference
in the wavelength of about $\frac{1}{10,000}$ %

In the band spectra of isotopes the difference must be even more
pronounced than in line spectra (*2*)   For the position of the lines
constituting the bands depends on the vibrations of the charged
atoms, and since these will be dependent on the moments of inertia,
they must also vary with the mass of the isotopes   In the case of
hydrochloric acid it has been calculated that for a band situated
in the infra-red, each line must be accompanied by a weaker associated
line displaced from the main line by $1.32\mu\mu$ As a matter of fact,
the associated lines have been found to exist experimentally, and
to be in good agreement with the predictions of theory

The examples cited here also confirm the idea that on all the
properties of the atom, with the exception of its mass and radio-
activity, only the charge of the nucleus and not its structure primarily
exerts an influence.   Conversely, we must also expect, from funda-
mental considerations, that the stability of the nucleus can be in-
fluenced by an alteration of the electron configuration, but that the
effect will be exceedingly minute   Corresponding to this we have the
fact that was established early in the history of radioactive research,
that the radioactivity of a chemical compound does not differ from
that of the radio-element contained in it.   The structure of the
nucleus can only be altered by a direct and successful attack on the
nucleus, of which we shall learn in Chapter XXI.

XVIII

ISOTOPY AS A GENERAL PROPERTY OF MATTER

IT has been made clear above that there is a simple genetic relation between the elements of the radioactive series , they are all descendants either of uranium or of thorium. As far as we have been able to establish directly, these elements are distributed over the region from the element with nuclear charge 92 (uranium) to that of nuclear charge 81 (thallium), whereby each of these places in the periodic classification is occupied by several isotopes The end-products of the disintegration series are types of lead (radium G, thorium D, actinium D), which neither emit rays that can be detected, nor are transformed into radioactive disintegration products On the assumption that RaG is stable we can calculate from geological data the amounts of this element in minerals (see Chapter XXVI), and these amounts are found to agree well with those actually found This fact, in particular, yields strong evidence in favour of the stability of RaG

Moreover, we have for some time been familiar with various reasons which render it probable that not only the radioactive elements, but all elements are closely related genetically. Of these we may mention the striking relations of the elements within the periodic classification, which have repeatedly given fresh support to the idea of a unitary constitution of matter. Moreover, a difference in atomic weights amounting to 4 units is frequently met with throughout the periodic classification, and this is completely intelligible in the region of the radio-elements, in consequence of the emission of a-rays. Apart from the radioactive substances between uranium and thallium, numerous attempts have been made to detect the emission of radiation from other elements. Only in the cases of potassium and rubidium has unequivocal evidence of radioactivity been obtained, whereas observations on the eventual radioactivity of elements like copper and zinc have not yet given conclusive results, owing to the widespread admixture of traces of radioactive substances, and the fact that it is impossible entirely to exclude the penetrating radiation from the earth and atmosphere

from such measurements. But when we bear in mind that the intensity of the activity depends on the shortness of the life of the element, and that we must assume (*vide* radioactive equilibrium) a long life in the case of elements available in large quantities, we should be wary in drawing conclusions as to the absolute stability of such elements * From the absence of a detectable radiation we can only decide upon a minimum value of the life of the element. But conversely, we are not justified in concluding that the rarest of the ordinary elements must be of short life and hence emit radiation   In such cases we must always consider the possibility that the reason for the sparseness of their occurrence may be due to their belonging to a branch of the main disintegration series, so that the proportionality between quantity and life no longer has validity. Thus protactinium, in spite of its considerable period, is present in smaller quantity than radium, which has a smaller period, but belongs to the main disintegration series of uranium   So that we cannot with certainty deny the possibility of a gradual transformation of the ordinary elements on the basis of measurements of their activity (3).

Now the phenomenon of isotopy is most intimately related with the occurrence of radioactive transformations.   Hence if we succeed in establishing that more than one type of the ordinary elements occurs in nature, we shall be justified in recognising in this fact an indirect argument for the possibility that transformation laws similar to those of the known disintegration series extend or at least have extended, throughout the whole region of the chemical elements † (4).   In the case of the radioactive elements and their end-products, isotopy has been established in two ways , first, by the observation that isotopes differ in the nature of their radioactive radiation, and secondly—in the case of the types of lead and thorium —by the detection of fluctuations in their combining weights   At first both methods failed in the case of the ordinary elements, which, as just mentioned, are not perceptibly active and which do not show

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* Were an element with a half-value period of only a few thousand years to disintegrate with emission of β- rather than of α-rays, it would be very difficult to detect its activity, particularly if it possessed a high nuclear charge number, in consequence of which the escape of the electrons would be rendered difficult

† At the same time, we must bear in mind that a development of the elements synthetically, by the aggregation of protons and electrons, could likewise lead to isotopes. We know nothing definite as to the manner in which the existing stable types of atoms have been formed.

PLATE IV.
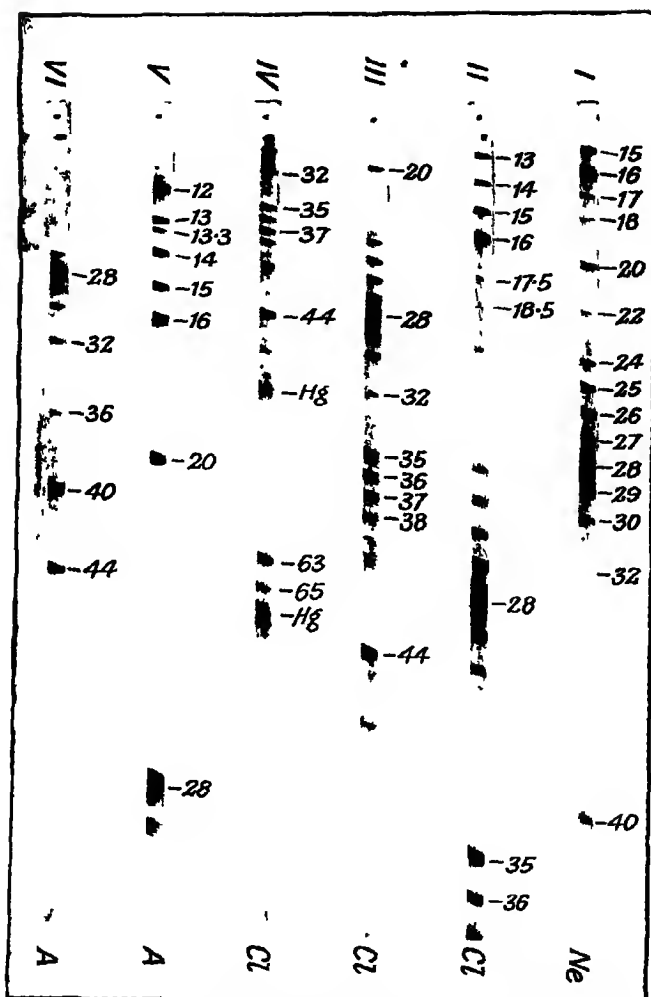
FIG. 33 (p. 135)
Mass-Spectra of the Elements Neon, Chlorine, and Argon

[It should be particularly noticed, in Spectra III and IV, that particles of mass 35 and 37, and likewise 36 and 38, are represented, corresponding to the atomic types Cl_{35} and Cl_{37}, and the molecular types HCl_{35} and HCl_{37}, but that there is no indication of particles of mass 35·46 (the combining weight of chlorine). In Spectrum V we observe a "second order line" at 20 and a "third order line" at 13·3, both of which, like the "first order line" at 40 in Spectrum VI, are due to argon. Line 36 in Spectrum VI, since it always accompanies the line 40, proves the definite existence of several per cent of $argon_{36}$ along with $argon_{40}$. In a similar manner we can read off the relevant atomic weights from the other spectra.]

the slightest variations in their combining weights, so far as can be recognised by the accuracy of atomic weight determinations hitherto attained   Quite constant results have been obtained for atomic weight determinations carried out with lead from very different lead minerals not containing uranium nor thorium; with copper, chlorine, and particularly with mercury from different geological epochs and districts (5); with iron, nickel and silicon (6) of terrestrial and cosmical origin; etc.   Not until the method of mass-spectroscopy had been devised and developed was it possible to establish that many of the ordinary elements are without doubt not pure elements, but mixed elements (see p. 143)   This method made it possible to determine the masses of the individual atomic types of an element present even in mixtures.

The method is based on the following principle (7).   The element to be investigated is subject to electric discharge in a highly evacuated tube, whereby its molecules and atoms in part assume one or more positive charges, and travel as " Positive Rays " towards the cathode   They pass through a slit in the cathode and so enter the investigation chamber   Here the particles are first deflected by means of an electric field, and then they are passed through a magnetic field so arranged that the deflection is now in the opposite direction.   Finally, they fall on a photographic plate.   By suitably choosing the strength of the magnetic and electric fields, by using suitable screens and a suitable position of the photographic plate, it is possible to attain that all the particles with a constant value of m/e are brought to the same place on the photographic plate, even when their velocities vary within a limited range   When particles with the same mass, and hence the same value of m, carry a double electric charge, they are deflected to another place on the photographic plate, viz   to the same place as would be all particles of mass $\frac{1}{2}m$ and charge e.   Corresponding to the terminology of ordinary spectroscopy, we designate the spectra so obtained as spectra of the first, second and higher orders   The values possessed by the individual lines, expressed as m/e, are found by comparison with the neighbouring lines of known atoms and molecules, such as C, CO, CO_2, O_2.   The sensitiveness of the method is so great that it is possible to recognise a mixture of isotopes in the proportion 99   1 as being a mixture of two types of atoms.

The accompanying mass-spectrogram (Fig. 33, Plate IV) gives an idea of the fineness of resolution obtainable in these mass-spectra.

From the intensity of the blackening of individual lines it is possible to draw quantitative conclusions as to the relative quantities of the constituent isotopes of an element present in the mixture.* This can be carried out with even greater accuracy by means of another mass-spectrographic method, of more limited applicability, which, in the place of the photographic plate, utilises the ionising action of the rays for the detection of the individual atomic types (9)

Table XXVII gives the results of mass-spectroscopy, so far as they have been hitherto established with certainty   In this table the atomic types of each element are arranged in descending order of the quantity present in the natural mixed element.   The doubtful isotopes are accompanied by a mark of interrogation

Within the limits of accuracy of the method, i e. on the average within about 0·1 %, practically all the atomic weights are whole numbers relative to $0 = 16$, hydrogen is the most conspicuous exception to this rule.   We further notice that even an element like bromine, the combining weight of which lies exceedingly near to an integral value, consists of two isotopes of different atomic weight.   Until all the inactive elements have been examined by this method it is futile to speculate on the relation between the elements as revealed by the present-day values of their combining weights, for these are sometimes only average values, and we are therefore not justified in ascribing to them the same significance as to the atomic weights, from the combination of which they are obtained.

We are immediately confronted by the question as to why a chemical element like chlorine, which consists of two isotopes, contains these constituents admixed so exactly in the same proportions that its combining weight has always been found to be constant, no matter how great the accuracy of the investigation (10).   The most probable explanation is that the formation of the chemical elements, apart from the known disintegration products of uranium and thorium, had already taken place before the consolidation of the earth's solid crust.   All the isotopes in the original liquid or gaseous mixture became homogeneously mixed in consequence of the practically complete identity of their properties, and it was these mixed elements of constant isotope-content that served to

* With boron it was even possible to deduce from the isotopic ratio that the combining weight of this element should be smaller than that officially recognised, and this result was confirmed later by direct chemical investigations (8).

TABLE XXVII

Atomic Types of the Elements

Ordinal Number.	Element.	Combining Weight.	Weight of Atomic Types.
1	Hydrogen - -	1·008	1 008
2	Helium - -	4 00	4
3	Lithium - -	6 94	7, 6
4	Beryllium - -	9 1	9
5	Boron - -	10 9	11, 10
6	Carbon - -	12·00	12
7	Nitrogen - -	14·008	14
8	Oxygen - -	16·00	16
9	Fluorine - -	19 00	19
10	Neon - -	20 20	20, 22
11	Sodium - -	23 00	23
12	Magnesium - -	24 32	24, 25, 26
13	Aluminium - -	26 96	27
14	Silicon - -	28 3	28, 29, 30 ?
15	Phosphorus - -	31 04	31
16	Sulphur - -	32 06	32
17	Chlorine - -	35 46	35, 37
18	Argon - -	39 9	40, 36
19	Potassium - -	39 10	39, 41
20	Calcium - -	40 07	40, 44 ?
21	Scandium - -	45 1	45
22	Titanium - -	48 1	48
23	Vanadium - -	51·0	51
24	Chromium - -	52 0	52
25	Manganese - -	54 93	55
26	Iron - -	55 84	56, 54
27	Cobalt - -	58 97	59
28	Nickel - -	58 68	58, 60
29	Copper - -	63 57	63, 65
30	Zinc - -	65 37	64 ?, 66 ?, 68 ?, 70 ?
31	Gallium - -	69 72	69, 71
32	Germanium - -	72 5	74, 72, 70
33	Arsenic - -	74 96	75
34	Selenium - -	79 2	80, 78, 76, 82, 77, 74
35	Bromine - -	79 92	79, 81
36	Krypton - -	82 92	84, 86, 82, 83, 80, 78
37	Rubidium - -	85 45	85, 87
38	Strontium - -	87·63	88, 86
39	Yttrium - -	88 9	89
40	Zirconium - -	91 3	90, 94, 92, 96 ?
47	Silver - -	107 88	107, 109
48	Cadmium - -	112 40	114, 112, 110, 113, 111, 116
49	Indium - -	114 8	115
50	Tin - -	118 7	120, 118, 116, 124, 119, 117, 122, 121 ?
51	Antimony - -	121 77	121, 123
52	Tellurium - -	127 5	128, 130, 126
53	Iodine - -	126 92	127
54	Xenon - -	130 2	129, 132, 131, 134, 136, 128, 130, 126 ?, 124 ?
55	Caesium - -	132 81	133
56	Barium - -	137 37	138
57	Lanthanum - -	139 0	139
58	Cerium - -	140 25	140, 142
59	Praseodymium - -	140 6	141
60	Neodymium - -	144 3	142, 144, 146, 145 ?
68	Erbium - -	167 7	164-176 ?
80	Mercury - -	200 6	202, 200, 199, 198, 201, 204
83	Bismuth - -	209 0	209

form the structure of our solid earth, and perhaps also of the other heavenly bodies (cf. what was said above as to the combining weight of meteoritic iron and nickel). At the same time, it must be emphasised in this connection that the results (particularly of the older atomic weight determinations) cannot lay claim to that degree of accuracy we should desire for the final decision as to the question of the constancy of the combining weights of the ordinary elements. For example, if we assume for simplicity that mercury consists of two types of atoms of weights 198 and 202, mixed in equal quantities with each other, a displacement of the mixture-ratio of 1 % in the course of time would not, of course, result in an equally large alteration of the combining weight , on the contrary, since the difference of the atomic weights only amounts to $\frac{1}{50}$ of the absolute value, it would only result in a displacement of the combining weight of $\frac{1}{10,000}$, which lies within the limits of error of most atomic weight determinations * Should such displacements in the constitution of the mixed elements of the above order of magnitude have occurred during the course of geological time, we could not hope by the usual methods to trace their effects in producing fluctuations in the combining weight We must also exercise the same caution with regard to conclusions that have been made as to the absence of an activity of the ordinary elements, which conclusions have been based on the constancy of the combining weights, hitherto always found confirmed. Nevertheless, especially in the case of mercury (*11*), it has not been possible to detect fluctuations even of 1 1,000,000, by means of the much more exact methods of density determination. Thus it is very improbable that this element is radioactive, and that its weighable isotopes have different disintegration velocities

* If, from each 100 atoms of weight 198, we assume one to be replaced by an atom of weight 202, the combining weight increases from $\dfrac{100(198+202)}{200} = 200$ to $\dfrac{99 \times 198 + 101 \times 202}{200} = 200\ 02$, or by one part in ten thousand.

SEPARATION OF ISOTOPES

As already mentioned, isotopes generally show differences in their atomic weights, sometimes by considerable amounts, thus RaB has an atomic weight of 214, and RaG 206, so that in this case we have a difference of 4 %. The reason why, until comparatively recently, isotopes yielded to none of the attempts to separate them is to be found in the fact that all the usual chemical methods of separation are based on the difference of electronic properties (solubility, vapour pressure, etc), and that for isotopes these properties are indistinguishably identical in consequence of their identical nuclear charge number. For their separation we can only avail ourselves of such methods as are based on the difference of nuclear properties. The number of these methods is quite small, and their applicability is still further limited by the fact that the effectiveness of the available differences is more or less paralysed by the superposition of foreign influences, under the conditions in which a separation might be practicable.

This applies to diffusion in the liquid state. If we carefully pour water over a solution containing the lead isotopes RaD-Cl$_2$ and RaG-Cl$_2$, both salts diffuse with the same velocity into the water, even though the lighter RaG ion has a greater molecular velocity. This property, which is favourable to rapidity of diffusion, is counteracted by the fact that the heavier RaD ion, in its frequent collisions with molecules of the liquid, is able to retain its direction of motion for a longer time than the lighter RaG ion, in consequence of its greater inertia. In gases, where the number of collisions is incomparably smaller than for liquids, this disturbing influence occurs in much lesser degree, and in this case it is actually possible to attain by diffusion a detectable displacement of the constitution of an isotopic mixture (*12*).

In addition to the *diffusion or effusion method*, the following methods of separating isotopes call for consideration. First, the utilisation of the different *density distribution in a gravitational*

field (13), and secondly, of the different *reaction velocity*, in particular the *velocity of volatilisation*. We shall now discuss the influence of a gravitational field.

It is well known that the heavy gas carbon dioxide is concentrated near the earth's surface, whereas in the farther reaches of the atmosphere we find a concentration of the lighter gas hydrogen. Similarly, for the two isotopes of neon (A W. 20 and 22), we should expect to find relatively more of the former than of the latter in the upper regions of the atmosphere, and this would constitute a partial separation of the two isotopes of neon. The application of the barometric formula for height indicates that at a height of 10 km the mixed element neon should no longer consist of 91 % $neon_{20}$ and 9 % $neon_{22}$, as at the earth's surface, but that it should now only contain about 8 % of the latter constituent. But this alteration in the composition of the neon is only to be expected if the distribution established by diffusion is not disturbed by streaming (convection), a condition which is only fulfilled in very limited measure, as is amply attested by balloonists. Instead of investigating the upper reaches of the atmosphere, we might also investigate the depths of the sea. Sodium chloride obtained from a depth of 10 km * should be richer in Cl_{37} and poorer in Cl_{35} than that found at the surface of the earth, the corresponding combining weight of the contained chlorine being 35 6 instead of 35 46. Here also, however, the ocean currents will produce very marked disturbances Centrifugal force calls forth the same effects as gravitational force, and a peripheral velocity of 1 km./sec corresponds to a difference in height of about 40 km.

The following consideration will serve as an illustration of the utilisation of different reaction velocities for the separation of isotopes *(14)*. If chlorine at reduced pressure passes through a silver tube, in such a manner that only a fraction of the chlorine molecules comes in contact with the walls of the tube, then in consequence of the greater molecular velocity of the lighter chlorine isotope relatively more of the latter than of the heavier constituent will reach the walls, and hence more $AgCl_{35}$ than $AgCl_{37}$ will be formed. As in the case of effusion, the concentration will take place here also in a measure which is inversely proportional to the square root of the molecular weights of the two types of chlorine. Instead of binding the chlorine chemically to silver, we might also freeze it

* The greatest ocean deep off Japan is just over 32,000 feet, i e 6 miles, or about the requisite depth, if we disregard convection currents.

out by making use of a suitably cooled glass tube in place of the silver tube. Moreover, we can volatilise chlorine under conditions such that every molecule that has once been volatilised can be prevented by chemical means or by freezing from returning to the liquid. This process is essentially different from that of a normal distillation, in which the vaporised molecules are very often cast back into the liquid before they finally escape, and in which, therefore, the difference in the velocity of volatilisation of the isotopes cannot be brought to account

Figure 34 illustrates an arrangement which has served to effect a partial separation of the isotopes of mercury by this method of " ideal distillation " About 300 cc of mercury are introduced into the flask H, the space between H and A is highly evacuated, and the flask A is then filled with liquid air The oil-bath C serves the purpose of heating the mercury to about 60° C. As a result of the greater volatilisation velocity of the lighter mercury isotope of atomic weight m_1, the amount of this which vaporises is at first $\sqrt{m_2/m_1}$ times as large as the amount of the heavier mercury isotope of atomic weight m_2, and the isotopic mixture that condenses on the cold surface A contains a correspondingly greater quantity of the lighter than of the heavier isotope. After the volatilisation of a fraction

Fig 34 Apparatus for the Partial Separation of the Isotopes of Mercury

of the mercury, the remaining " heavy ' fraction is removed by the evacuation of E, and by opening the taps D and G. We now allow the liquid air to evaporate from A, when the solid distillate melts, and drops from the walls of A into the vessel H, whence it is removed in the same way as was the heavy fraction previously. By successive repetitions of this process it has been possible to prepare two kinds of mercury, the densities (14) of which differed by 0 05 %, corresponding to a difference in combining weight (15) of 0 1 of a unit.

By means of the same method it has also been possible to prepare

two kinds of chlorine (about 20 gm. of each), the combining weights of which differed by more than 2 units in the second decimal place. These different kinds of chlorine were obtained by " ideal " evaporation of an aqueous solution of hydrochloric acid of about seven times normal strength, and condensation of the vaporised mixture of water vapour and hydrochloric acid on a surface cooled by liquid air (*16*).

Owing to the fact that with advancing separation the yield decreases, none of the methods of concentration mentioned is suitable for the production of the isotopes in a completely pure state. In order to obtain a complete separation we might produce ions of the isotopes, say, in a positive ray tube, and then separate them by deflection in a magnetic and an electric field, as in the mass-spectrograph.   For the time being, however, the development of this analytical method into a preparative one is frustrated by experimental difficulties.

Once isotopes that occur separately in Nature have been completely and uniformly mixed with each other, and this is only possible in the liquid, solution or gaseous states, it is as impossible to separate them again by simple methods as it is to separate those which occur already mixed in natural deposits   Apparent separations can always be attributed to the fact that the condition of complete and uniform mixing has not been satisfied.   Thus it has been observed that the ratio of ThB to ThC is greater than that of RaB to RaC when these four radio-elements are simultaneously adsorbed by ferric hydroxide (*17*).   The explanation of this behaviour is undoubtedly that the radio-elements were partly only in colloidal solution, and that the transition into the state of molecular dispersion had only proceeded slowly, with a completeness differing in accordance with the life period of the radio-elements   Consequently, during the process of adsorption, which is always particularly strong with colloids, the ferric hydroxide encountered a different ratio of the colloidal and molecularly dispersed fractions of the products of the thorium and radium families respectively. Hence, even in this case, the condition of uniform mixing was not fulfilled

MIXED ELEMENTS AND PURE ELEMENTS. COMBINING WEIGHTS AND ATOMIC WEIGHTS

THE extensive independence of chemical and spectral properties on atomic mass results in our being able to consider an isotopic mixture as a single element for all practical purposes. In the formula of mass action, etc., we simply require to insert the sum of all the isotopic atoms or molecules for the concentration of the element concerned and its compounds Should the relative amounts of the isotopic atoms change, this alteration will not be noticeable with regard to the chemical mass action, the electro-chemical potential, and so on, but we should have to ascribe to the element involved another combining weight

We have already had occasion to discuss the fluctuations in the combining weight of lead obtained from different sources (see p 110). From a chemical or spectroscopic point of view, however, the types of lead referred to are unitary elements, the purification and the determination of the " atomic weight " of which could be carried out with precision by the usual methods An element consisting of different isotopes is termed a " *mixed element* "—an expression that we have already used—and it is preferable to speak of its " *combining weight* " rather than of its atomic weight Thus the respective weights of the atoms contained in chlorine are 35 and 37, which numbers differ from its combining weight 35 46 An element which consists of only one type of atoms is called a ' *pure element.*" It is associated with a constant *atomic weight*, which directly indicates the weight of its atoms relative to oxygen $= 16$

When we speak of a " chemical element " in general, it is not clear whether we are dealing with a pure element, or with a mixed element, as in the case of, say, mercury and chlorine. The mixed elements mentioned are composed of isotopes. and these cannot be separated by the usual chemical methods of separation But, as we have seen in the previous chapter, they can be more or less

completely separated by various physical processes.   Consequently, we can no longer define a chemical element as a substance which cannot by any means be broken up into simpler substances.   The following may be regarded as a convenient " practical definition " (*1*) : *A chemical element is a substance which cannot be resolved into simpler substances by any chemical process.*   For all practical purposes the chemical inseparability of isotopes retains its validity, and this is the sole reason why chemistry is obliged to adhere to the old elements as the constituent bricks of its chemical system.   Moreover, for practical and didactic purposes the above definition is also sufficiently precise, since all the successful methods of separating isotopes are typically mechanical ones, inasmuch as in them we always make use of the differences in mass and never of the differences in chemical properties   When substances enter into no chemical reactions whatsoever, as in the case of the rare gases, it is of course not possible to apply the criterion of chemical inseparability, and we must test the unitary nature of the nuclear charge (cf the definition below) by other methods such as spectroscopy.   But it was the impossibility of chemically resolving elements like gold, mercury, etc., and not the exceptional cases of the rare gases that led to the formulation of the chemical conception of an element.   Even to-day, exactly as at the time of its conception by Boyle (*2*), its value lies in the fact that " corpuscles of a compound nature may *in all the wonted examples of chymists* pass for elementary "*

A more exact and more " theoretical definition," even though it is more removed from the chemical meaning of the conception of an element, can be given by having recourse to the ideas of atomic theory   We may say, quite rigorously ·

A chemical element is a substance, all of the atoms of which have the same nuclear charge   Examples · hydrogen (nuclear charge 1), chlorine (nuclear charge 17), lead from an arbitrary mineral (nuclear charge 82), lead from disintegrated radium emanation (nuclear charge 82)

* The above-given definition also enables us to recognise immediately that there is no reason, for example, in regarding the successful disruption of the nucleus of an aluminium atom (see next Chapter) as ground for excluding this substance from the list of the chemical elements, for the method of resolution applied was not a chemical one.   We can be quite certain that in all chemical reactions we do not encounter the disruption of atoms nor the separation of isotopes.   Hence the composite nature of the elements, which is present in a dual sense, can be disregarded in chemistry.

TABLE XXVIII

Atomic Numbers and Combining Weights of the Chemical Elements

Atomic Number	Name of Element.	Symbol	Combining Weight	Atomic Number	Name of Element.	Symbol	Combining Weight.
1	Hydrogen	H	1 008	47	Silver	Ag	107·88
2	Helium	He	4 00	48	Cadmium	Cd	112 40
3	Lithium	Li	6 94	49	Indium	In	114 8
4	Beryllium	Be	9 1	50	Tin	Sn	118 70
5	Boron	B	10 8	51	Antimony	Sb	121 77
6	Carbon	C	12 00	52	Tellurium	Te	127 5
7	Nitrogen	N	14 008	53	Iodine	I	126 92
8	**Oxygen**	**O**	**16 000**	54	Xenon	X	130 2
9	Fluorine	F	19 00	55	Caesium	Cs	132 81
10	Neon	Ne	20 2	56	Barium	Ba	137 37
11	Sodium	Na	23 00	57	Lanthanum	La	139 0
12	Magnesium	Mg	24 32	58	Cerium	Ce	140 25
13	Aluminium	Al	27 1	59	Praseodymium	Pr	140 9
14	Silicon	Si	28 3	60	Neodymium	Nd	144 3
15	Phosphorus	P	31 04	61	—	—	—
16	Sulphur	S	32 07	62	Samarium	Sa	150 43
17	Chlorine	Cl	35 46	63	Europium	Eu	152 0
18	Argon	A	39 88	64	Gadolinium	Gd	157 3
19	Potassium	K	39 10	65	Terbium	Tb	159 2
20	Calcium	Ca	40 07	66	Dysprosium	Dy	162 5
21	Scandium	Sc	·45 1	67	Holmium	Ho	163 5
22	Titanium	Ti	48 1	68	Erbium	Er	167 7
23	Vanadium	V	51 0	69	Thulium	Tm	169 4
24	Chromium	Cr	52 0	70	Ytterbium	Yb	173 5
25	Manganese	Mn	54 93	71	Cassiopeium	Cp	175 0
26	Iron	Fe	55 84	72	Hafnium	Hf	178 6
27	Cobalt	Co	58 97	73	Tantalum	Ta	181 5
28	Nickel	Ni	58 68	74	Tungsten	W	184 0
29	Copper	Cu	63 57	75	Rhenium	Re	—
30	Zinc	Zn	65 37	76	Osmium	Os	190 9
31	Gallium	Ga	69 72	77	Iridium	Ir	193 1
32	Germanium	Ge	72 5	78	Platinum	Pt	195 2
33	Arsenic	As	74 96	79	Gold	Au	197 2
34	Selenium	Se	79 2	80	Mercury	Hg	200 6
35	Bromine	Br	79 92	81	Thallium	Tl	204 4
36	Krypton	Kr	82 92	82	Lead	Pb	207 20
37	Rubidium	Rb	85 45	83	Bismuth	Bi	209 0
38	Strontium	Sr	87 63	84	Polonium	Po	(210)
39	Yttrium	Y	88 9	85	—	—	—
40	Zirconium	Zr	91 3	86	Radon	Rd	(222)
41	Niobium	Nb	93 5	87	—	—	—
42	Molybdenum	Mo	96 0	88	Radium	Ra	226 0
43	Masurium	Ma	—	89	Actinium	Ac	(226)
44	Ruthenium	Ru	101 7	90	Thorium	Th	232 15
45	Rhodium	Rh	102 9	91	Protactinium	Pa	(230)
46	Palladium	Pd	106 7	92	Uranium	U	238 2

A pure element is an element that consists of only one type of atoms.
Examples : hydrogen (atoms of weight 1·008), lead from radium
emanation (atoms of Radium D—emitting β-rays—of weight 210).

A mixed element is an element that consists of several types of atoms.
Examples : chlorine (atoms of weight 35 and 37), lead from purest
uraninite (atoms of RaG of weight 206, atoms of AcD of weight 206,
atoms of RaD of weight 210, the last emitting β-rays).

The question as to whether a chemical element is a pure or a mixed
element is of no practical importance to the chemist.   He is con-
cerned only with the combining weights of the elements, and not
with the weights of the individual types of atom.   Although the
complete " Table of Atomic Types " is of service for scientific
purposes, it is preferable to retain the long-established " Table of
the Chemical Elements," as it is shorter and gives a clearer survey
of the elements.   Certain " Atomic Weights Committees," *e.g.* that
of the German Chemical Society, publish both Tables annually.   As
we have already collected together the atomic types of the radio-
elements in Table XXIII (p. 112), and, as far as they are at present
known, those of the inactive elements in Table XXVII (p. 137), we
shall present here only a " Table of the Elements and their Com-
bining Weights," arranged in the order of their atomic numbers
(Table XXVIII, p 145)

XXI

DISRUPTION OF THE CHEMICAL ELEMENTS

UP to the present we only know of one method that permits us to resolve the nuclei of the atoms artificially, and thus to achieve the aspiration of the alchemists, namely, the transmutation of the elements. It consists in subjecting the elements to the action of penetrating a-particles, and the amounts hitherto transformed have been exceedingly small.

Thus if we project the a-particles from radium C into a vessel containing pure nitrogen, we can detect the production of charged hydrogen atoms of high velocity. The resulting quantities of hydrogen are much too small to be detected by chemical means, for on the average 100,000 a-particles liberate only one hydrogen atom. We can obtain proof that we are here dealing with hydrogen by deflection experiments in magnetic and electric fields, in much the same way as the identity of a-particles and helium atoms was recognised (see p 19) In this manner it has been shown that the particles have unit mass and unit charge. These hydrogen particles must be derived from the atoms of nitrogen struck by the a-particles. In the first place, special experiments have shown that the presence of hydrogen as an impurity in the nitrogen used would only result in much smaller effects than have been observed with pure nitrogen, owing to the rarity of a favourable collision between a-particles and this rarified hydrogen. Secondly, the velocity possessed by the H-particles is so exceedingly great that the energy necessary to produce them could not be derived solely from the colliding a-particles. It is true that when we bombard pure hydrogen with a-particles we also obtain H-rays, but their initial energy is very much smaller. By observation with a zinc sulphide screen it can be shown that in this case the range of the H-rays amounts to only 29 cm. at atmospheric pressure, which agrees with the value to be expected theoretically, whereas the H-rays produced in nitrogen have ranges up to 40 cm Moreover, H-rays derived from disrupted elements are emitted in all directions, whereas the H-particles obtained by

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bombarding hydrogen and its compounds with α-particles are practically restricted to the original direction of the α-particles (3). Accordingly, with nitrogen, the sole place of origin of the H-rays is to be looked for in the nitrogen atoms   They must originate in the nuclei of these atoms, since this is the only place where matter exists within the atom, and this fact also explains their large energy. For we can readily imagine that as a result of the impact of α-particles the forces bound up within the atomic nucleus become just as free as in the case of radioactive disintegration, where they are also revealed.   This emission of H-rays under the action of α-particles, first observed with nitrogen, is also shown by a number of other elements, and in a most striking manner by aluminium, with which H-rays have been observed up to a range of 90 cm.   Here also several hundreds of thousands of α-particles require to be shot into the element in order to produce one such rapid H-particle.   It can be calculated that it would be necessary to allow 1 gm. of radium to project its rays into aluminium for a period of 3000 years in order to produce only 1 mm ^{3} of hydrogen in this manner.   From this we see that this method of transmuting elements is still far from being of any practical importance.

The work on the disruption of the nitrogen nucleus has recently been extended in an interesting manner by the cloud expansion method (4).   This is illustrated in Fig 35 (Plate V), the two photographs having been taken simultaneously, and in perpendicular directions. The faint track of the ejected proton is discernible as well as the pronounced track of the recoiling nucleus, but there is no indication whatever of the α-particle after its collision   It seems certain that the incident α-particle becomes swallowed up by the nitrogen nucleus.   In such a case we are led to the conclusion that the result of the loss of a proton, and the capture of an α-particle by the nitrogen nucleus must be the formation of a new nucleus of atomic number 8 and mass 17.   Other evidence points to the possibility of such an occurrence, which is in this case nothing less than the artificial integration of an isotope of oxygen from nitrogen. α-particles from ThC were used in these experiments.

The following Fig 36 shows that, in addition to nitrogen and aluminium, several other elements have already been disrupted by α-particles.   Moreover, the H-particles ejected from elements of odd nuclear charge number have in general greater ranges than those ejected from elements of even nuclear charge number (5).

PLATE V.

Fig 35 (p 148)
Ejection by an a-Particle of a Proton from a Nitrogen Nucleus

Fig 38 (p 191)
Writing on a Photographic Plate by means of Radium

Apart from those mentioned in the figure, it is probable that a number of other elements are capable of disruption (*6*), but the relevant experiments have not yet been completed.

In most of the experiments previously mentioned, the α-particles of RaC' of range 7 cm. were used. The smaller the velocity of the particles, the poorer is the yield of H-rays From this we may conclude that attempts to disrupt atomic nuclei by means of β-particles will have little chance of success until we are able to produce them with a velocity corresponding to 6 millions of volts. For
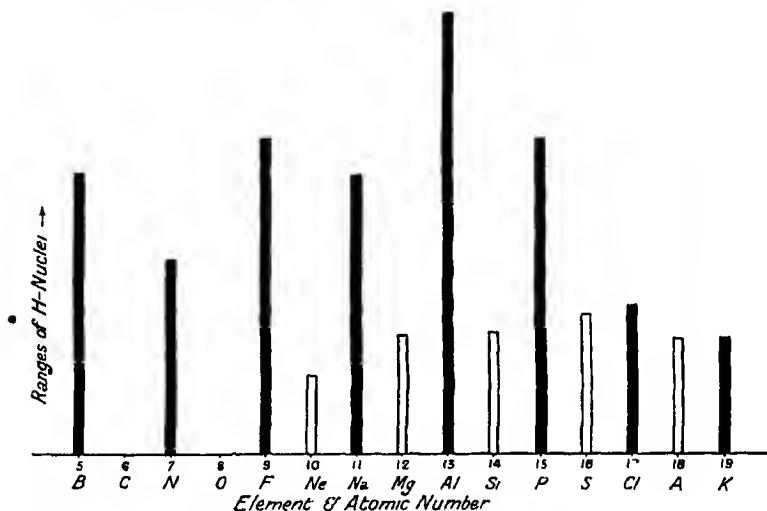
Fig. 36   H Particles resulting from α-Bombardment

purposes of comparison, it may be recalled that a potential of 2,200 volts is already sufficient to liberate an electron from the innermost electron-ring of aluminium.

The explanation of the poor yield of H-rays is to be found in the fact that always only a very small fraction of the α-particles can penetrate to the nucleus of the atoms to be disrupted Coulomb's law retains validity even in close proximity to the nucleus, and this results in a repulsion of the α-particles (see p. 28). On the assumption of the validity of this law, we can calculate the frequency and distribution of the sudden deflections experienced by α-particles in their passage through air. A comparison with the values found experimentally (see Fig. 25, p. 78) reveals such a close agreement that we can infer that Coulomb's law retains validity between $3 . 10^{-12}$ cm. and $3·7 . 10^{-10}$ cm. (*7*).

The emission of H-rays takes place not only in the direction of the incident α-particles, but also in the opposite direction. This, too, supports the view that the escaping H-particle owes a large part (about 40 %) of its energy to an explosion of the nucleus, and that in this explosion the α-particle plays the part of a kind of trigger (8).

Experiments performed with the object of deciding whether bombardment with α-particles causes the atoms of the ordinary elements to become unstable and radioactive have led to a negative result. In this connection it has been established experimentally that when metals are bombarded by α-particles, they do not acquire an induced activity with emission of mass-particles which persists after 10^{-4} sec. Mass-particles of 2 mm. range or more would have been detected in these experiments (9). Similar attempts to influence the velocity of transformation of uranium and radium D, by subjecting them to the action of radiation, have also led to a negative result (10).

XXII

STRUCTURE OF THE ATOMIC NUCLEUS

THE study of radioactive phenomena has taught us that, within the nuclei of the heavy atoms, some of which emit α-rays, there must be helium nuclei. This is in agreement with the fact that the difference in the atomic weights even of light elements—in general, of two elements that are not immediate neighbours—frequently amounts to four units. For example, in round numbers, we have $C = 12$, $O = 16$, $Ne = 20$, $Mg = 24$, $Si = 28$, $S = 32$; we may thus reasonably assume that they also contain helium as a structural unit. But since the difference between successive elements often amounts to only 1 or 3, it seems necessary to conclude that the nuclei of composite atoms also contain a lighter constituent. Hydrogen is the only element known to us that fulfils this condition, and hence it alone calls for consideration. The experiments on atomic disruption mentioned in the previous chapter constitute a confirmation of this view, which has long been looked upon with favour.

Apart from the positively charged nuclei of hydrogen and helium, the occurrence of β-rays proves (see p 72) that the nuclei of radioactive atoms also contain a certain number of electrons, so that the nuclear charge is equal to the algebraic sum of the positive and negative units of charge available within the nucleus. We can state with certainty that in the uranium nucleus, for example, there must be at least 6 electrons, corresponding to the 6 β-raying daughter elements UX_1, UX_2, RaB, RaC, RaD and RaE. A comparison of the atomic weights with the nuclear charge numbers shows, however, that the number must be much greater, for if the heavy atom concerned were only composed of helium nuclei (mass $= 4$, charge $= 2$), the nuclear charge numbers would always amount to one-half of the atomic weights. But from the atomic weight 40 upwards the charge begins to lag behind this value, and this makes it probable that in the succeeding positions in the periodic classification electrons enter into the structure of the nucleus. It is estimated that

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the heavy radio-elements probably contain from 20 to 30 electrons. Thus thorium has an atomic weight of 232 and an atomic number 90 ; on the assumption that the thorium nucleus consists of 58 helium nuclei, which corresponds to 116 positive charges, it follows that we must postulate the existence of 26 electrons in the nucleus (*11*), since the effective nuclear charge is only 90. If the thorium nucleus contains H-nuclei in addition to He-nuclei, we obtain a still greater number of nuclear electrons, since for hydrogen the ratio of the charge to the mass is twice as large as for helium

It has also been possible to form more detailed ideas as to the manner in which the nuclear electrons are arranged. In the radio-active disintegration series we frequently find that an α-rayer is succeeded by two β-rayers, or a β-rayer by an α- and a β-rayer. This makes it probable that in the nuclei of radioactive atoms there are groups consisting of one helium nucleus and two electrons, and that these groups become unstable when they lose one of their constituent parts, so that the other two components of the group will also be ejected very soon after. At other places in the disin-tegration series we meet with a succession of several α-rayers. From this fact we may draw the conclusion that groups of helium nuclei devoid of electrons also occur in the nucleus, and these, once they have become unstable, likewise eject all their component parts before the disintegration passes over to another such group within the nucleus. We may denote He-nuclei neutralised by two electrons by the symbol α', the associated electrons by β, the helium nuclei with a free charge by α, the neutralised hydrogen nuclei by H, and the electrons neutralising them by e. We can now say that the α'-particles and the H-particles are instrumental in making the atomic weight of the heavy elements greater than twice the atomic number. By way of illustration, the nucleus of uranium (atomic weight $= 238 = 59 \times 4 + 2$, atomic number $= 92$) could be constructed of the following N constituent parts :

$$N = 46\alpha + 13(\alpha' + 2\beta) + 2H + 2e$$

It may be mentioned that the differentiation between α and α'-particles in the nucleus also enables us to understand certain characteristics of dual disintegration (*12*).

We have no exact information (see, however, p. 151 above) about the forces which hold the positive particles and the electrons together in the nucleus of the stable atoms, nor of the processes which lead to radioactive disintegration (see p. 153). Certain regularities

are noticed when we compare isotopes, *i.e.* atoms of the same nuclear charge number (*13*). We then find that the tendency to β-disintegration is greater and to α-disintegration less, the higher the electron content of the atom, or the greater the lag of the nuclear charge number behind the semi-atomic weight. In other words, for the types of one and the same element, the β-decay is stronger for those of high atomic weight, whilst the α-decay is stronger for those of low atomic weight; *e g.* of the types of lead which emit β-rays, RaB (atomic weight = 214) is shorter lived than RaD (atomic weight = 210), and of the types of uranium emitting α-rays, uranium I (atomic weight = 238) is of longer life than uranium II (atomic weight = 234).* Moreover, when two consecutive β-ray transformations occur, the second is the more rapid of the two

A second rule which gives us some information about the stability of the radioactive atoms is the relation, already mentioned, between the range and the velocity of disintegration (see p. 106) Accordingly, we are able to form a conclusion as to the stability of the radioelement concerned, by considering the energy with which the α-particles are emitted. There is hope that we may gain some insight into the mechanism of radioactive disintegration by the aid of these rules, which are at present purely empirical ones.

It is not improbable that (*14*) with increasing atomic number the dimensions of the nuclei increase so rapidly that the interaction between parts of the nucleus and the planetary electrons may exercise an important influence, and that the radioactive elements lie precisely in this region.

The readjustment of the atomic nucleus as a result of the process of disintegration always involves a considerable diminution of the inner energy content of the atom. Thus the energy content of an atom of RaEm is roughly 10^{-13} cal. smaller than that of a Ra atom ; when it is calculated for one gram of the elements, this difference amounts to about 10^9 calories.

According to the theory of relativity, the mass of a body appears to be greater when its energy content increases, and conversely.†

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* Polonium, and individual members of the actinium series, are exceptions to this rule.

† One of the most important results of the theory of relativity states that the simple relation $M = \dfrac{E}{c^2}$ exists between the energy content (E) and the mass (M) of a system, where c denotes the velocity of light.

Whereas the energy changes involved in chemical processes are insufficient to call forth appreciable alterations in mass, the above diminution in energy is so considerable that it must suffice to reveal itself in a detectable decrease in the mass of the element. Thus, in the production of radium from uranium, in addition to the diminution of mass by 12 units resulting from the loss of three a-particles, we have a diminution of 0·02 units in consequence of the energy loss of the atom.* In addition to the cause (the occurrence of a mixed element) discussed in Chapter XVIII, we have here a further reason for the deviation of combining weights from whole numbers. The investigation of mass spectra described on p. 136 has furnished proof that both hydrogen and helium are pure elements. In spite of this, the ratio of the atomic weights of these two substances is not a whole integer, but is equal to $\frac{4}{1·004}$. This can only be due to the fact that the energy content of the 4 hydrogen nuclei (protons) in the helium nucleus is distinctly less than four times the energy content of the single hydrogen nucleus contained in an atom of hydrogen. It can be calculated that the quantity of energy which could be obtained from the transformation of 1 gm. of hydrogen into helium amounts to the extraordinarily large value of $1\,66 \cdot 10^{11}$ calories. In order to derive this amount of heat from the combustion of hydrogen, with attending production of water, we should have to burn 5,000 kgm. of hydrogen.

The influence exercised by the nature of the arrangement of the various protons and electrons on the energy, and thus on the mass of the nucleus, is often called the effect of packing. The atomic weights of the pure elements are thus whole numbers only when we can disregard this effect of packing (15).

The prevalence of the elements in Nature is determined by their nuclear structure. The nuclei of the atoms of atomic number up to 28 are particularly stable. More than 99·9 % of all the matter in analysed meteorites has been found to consist of these light elements, and the crust of the earth is also mainly composed of them. Of these light elements, the ones that are most strongly represented are those which, according to their atomic weights, can be regarded as being built up solely from He-nuclei (more than 90 %). Moreover,

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* The difference between the experimental atomic weights of uranium and radium is not exactly 12, but $238\,18 - 226\,0 = 12\,18$. This difference is not adequately explained by means of the above-mentioned cause. In this connection, see p. 174.

elements of odd nuclear charge are rarer than the two neighbouring elements of even nuclear charge, and this regularity appears to hold valid throughout the periodic classification (*16*). This points to a greater instability of elements of odd nuclear charge, a result which is fully borne out by the experiments on nuclear disruption (see p. 149).

THE PREPARATION OF RADIOACTIVE SUBSTANCES

IT will be clear from what has already been said about the chemical nature of the radioactive substances that they do not constitute a group of elements with the same, or even with similar chemical properties. Their physical behaviour, *i.e.* the disintegration of their atoms, is the only thing they have in common. From the chemical point of view they differ greatly from one another, and this applies even to elements such as radium and radium emanation which are very closely related genetically. It follows, then, that no single process can be applied to the production of one and all of them, and it is not possible to state certain group reactions as in the case of the rare earths or the alkali metals.

Moreover, owing to their radioactivity and consequent instability, we are here faced with special difficulties such as we meet with in no other branch of chemistry An inactive substance that has once been freed from foreign chemical elements remains permanently pure, provided it is suitably stored. It would strike a chemist as being very remarkable if chemical elements that he had carefully removed were to make their appearance again after the course of a few days or weeks. But with radioactive substances this is always occurring, with some more quickly than with others Of course, when the re-formation occurs after an interval of a few hours or a few minutes, the amounts formed in this time are never weighable nor visible, but are only rendered evident by the radiation they emit. In the ordinary chemical sense the preparations have remained pure, and it is impossible to recognise the admixture of a foreign element either by means of reagents or with the aid of a spectroscope. Nevertheless, the electroscope reveals to us that the substance which had been removed is again present in the material.

In the preparation of radioactive substances in a state of purity it is therefore necessary to differentiate between the terms "chemically pure" and "radioactively pure." The methods we apply will differ greatly according to the purpose we have in hand.

" Chemically pure " thorium, to take one example, may contain a number of radioactive disintegration products as impurities, without its utility being adversely influenced. Conversely, a preparation of radium which is pure from the radioactive point of view (e.g. free from mesothorium) may, for many radiological investigations, contain quite appreciable quantities of barium. In the chemical sense, we can obtain only very few of the radioactive substances in the pure state ; besides uranium and thorium, only protactinium, radium, radium emanation and radium D can be obtained in visible quantities. Nevertheless, we are rarely concerned with the chemical purity of these substances, for their most valuable feature is their radioactive properties, which lose little or none of their effectiveness by the admixture of inactive material. Thus chemically pure radium chloride (i e 100 %) has hitherto only been prepared on two occasions, namely, in Paris and Vienna, and that for scientific purposes. We also rarely require complete purity in the radioactive sense, for an " impurity," particularly of the disintegration products of the substance itself, is quite welcome in practice, because in this way the activity of the substance (e g. mesothorium or radiothorium) is increased. In scientific investigations, however, the radio-chemist is frequently confronted by the task of preparing the pure substance. But it will be clear from what has been said that in this case he must be informed exactly as to the day and hour on which the " radioactively pure " preparation is desired, and he will then so arrange his work that the short-lived, and hence quickly regenerated disintegration products are removed immediately before use is made of the preparation.

A second difficulty met with in the preparation of pure radio-active substances lies in the fact that many, in fact most of the radioactive substances, cannot be separated chemically from other partly active and partly inactive substances, once they have been mixed, either during their preparation or in consequence of their occurrence together in Nature. This difficulty is a much more disagreeable one, because it is capable of making impossible the practical utilisation of the radioactive substance. These disturbing elements are isotopes of the substance concerned (see Chapter XII). For example, RaD, in spite of the relatively large quantity of it which occurs in minerals, and although its chemical properties are quite accurately known, cannot be obtained in concentrated form—in which form it would be very useful for many purposes—because its

chemical properties are identical with those of the other types of lead with which it is associated in uranium minerals. We now know that the phenomenon of isotopy is one which also occurs with numerous inactive elements, but in this case the problem of the separation of the isotopes manifests itself in quite another form. Here we require the separation of the old chemical elements into fractions differing from each other solely in their atomic weights, a task the solution of which is sought for mainly because of its theoretical importance. But with the radio-elements the individual atomic types of the elements are characterised by particularly interesting and valuable properties, namely, by their radiations, and hence the problem of the separation of isotopes here appears in the form of the preparation of the radioactive substance concerned in the " pure state "

A third and final difficulty met with in the isolation of the radio-elements has its origin in the short life of some of them. When they disappear in fractions of a second, it is clear that we cannot obtain them by chemical manipulations (by precipitation, filtration, etc.) ; but even those which live for several minutes or hours cannot generally be isolated chemically from such a complicated mixture as we meet with in most uranium and thorium minerals. But we can avoid this difficulty, for the quicker an element decays, the more rapidly it is re-formed from its parent substance also. Correspondingly, the general principle involved in the preparation of short-lived substances consists in separating the parent substance from the mineral in as concentrated a form as possible. Or should this parent substance also be too unstable, we should separate a more stable and earlier member of the disintegration series. We can then await the growth of the desired product, and then undertake the chemical separation in a manner which is both easy and quick. Table XXIX gives a summary of the radio-elements which, in consequence of their long half-value periods (T)—also given in the table—can be extracted directly from the minerals. They are arranged in the table in order of decreasing half-value period, and the last five can also be obtained from their parent substances, just as in the case of the typically " short-lived " ones. Under favourable circumstances this is a particularly easy process in the case of RaD, for one of its more distant ancestors, radium emanation, is easily prepared in the pure state, and the intermediate products are all short-lived.

Table XXIX

Radio-elements of Long Life, which can be extracted directly from the Minerals

Thorium	-	$T = 1.5 \quad 10^{10}$ years.	Actinium	-	$T = 20$ years
Uranium	-	$5 . 10^9$,,	*Radium D	-	ca. 20 ,,
*Ionium	-	10^5 ..	*Mesothorium 1		6·7 ,,
Protactinium		10^4 ,,	*Radiothorium		1·9 ,,
Radium	-	1580 ,,	Polonium	-	136 days

Those elements denoted by * cannot be obtained directly as pure elements, owing to the fact that the minerals contain isotopes of longer life.

In what follows we shall give separate accounts of the most important facts concerning the preparation of the long-lived and short-lived radio-elements.

A. Preparation of the Radio-elements of Long Life

Thorium —Since large quantities of very pure thorium are required in industry, quite a number of processes for the extraction of " chemically pure " thorium are known   But we shall not deal with them here, because fuller information can be obtained from text-books on Chemistry and particularly from the special works on the rare earths   It should be mentioned here, however, that the thorium obtained by the usual processes is never " pure from the radioactive point of view." but is contaminated at least by its isotope radiothorium   But there is a means of separating it even from this radio-element, and we propose to deal with it, since it is instructive to see how the chemist, by taking time into his confidence, can carry out purifications which would be impossible by direct means.   The radiothorium contained in thorium after its chemical purification decays to an almost negligible fraction of its former value after the lapse of 20 years , but during the same time mesothorium 1 is formed from the thorium, and from this fresh radiothorium is produced.   By adding barium to the solution and separating the thorium from it, and frequently repeating this process throughout the twenty years, we can ensure that appreciable quantities of mesothorium can never accumulate in the thorium solution.   During this period the old radiothorium has completely disappeared and no fresh radiothorium has been regenerated, so that we now have not only the chemically pure thorium salt, but it is also

pure from the radioactive point of view. In order that this may be successful, however, it is necessary that the thorium mineral should contain only very small amounts of uranium, so that the separated thorium will be contaminated with the merest traces of the long-lived isotope ionium. Monazite sand is used almost exclusively as the source of thorium. The best known thorium minerals are thorite and thorianite. (See also Table XXXIII, p. 219).

Uranium —We do not propose to enter into the question of the preparation of chemically pure uranium salts either, since the necessary instructions are easily found in chemical literature. In contrast to thorium, we cannot obtain uranium as a " pure element," no matter what artifice we may adopt. Since uranium II, which is isotopic with uranium I ($T = 5 \cdot 10^9$ years), possesses a large half-value period, $T = 2 \cdot 10^6$ years, it is impossible to wait till it has decayed. But for all practical purposes, the " mixed element " uranium (*i.e.* as regards the magnitude of its combining weight, etc) consists only of uranium I; owing to the large difference in their life periods only about one atom of uranium II is associated with 3.000 atoms of uranium I. Pitchblende is the chief mineral used in the manufacture of uranium. (For additional uranium minerals, see Table XXXIII, p 219)

Radium.—In all unaltered primary uranium minerals about $3 \cdot 4 \cdot 10^{-7}$ gm. of radium are associated with 1 gm of uranium (*1*). Correspondingly, we only find about 2 gm. of radium in 10,000 kgm. of a uranium pitchblende. Its extraction is, of course, a very tedious task, but it is not disturbed by the presence of any isotope of radium, and it is due to this happy circumstance that the first attempt to extract radium from pitchblende residues was crowned with complete success. This work was carried out by M. and Mme. Pierre Curie. Since the chemical properties of radium are very closely related to those of barium, we can apply any process which permits of a quantitative and rapid separation of the barium from the remaining constituents of the mineral   It is not possible to give a definite and generally valid procedure for the extraction of the radium, because the initial materials require different treatment. Moreover, the price of radium is not high enough to justify the rejection of the other valuable constituents of the mineral, without endangering the business aspect of the process. Thus the uranium content, for example, is about one third as valuable as the radium content, and when vanadium is present, it must always be extracted. Neverthe-

less, in all the processes, we can differentiate roughly between the following main steps in the extraction :

(1) Solution or working up of the uranium minerals.

(2) Separation of all sulphates insoluble in water.

(3) Their conversion into soluble salts.

(4) Purification of the radium and barium from foreign constituents

(5) Fractional enrichment of the radium in the barium.

Each of these points can be widely varied.   We do not propose here to enter into the numerous suggestions and experiments on this aspect of the subject   We shall content ourselves with the discussion of two processes that have been well tried on the large scale, and which differ greatly both in the methods adopted and in the starting-off material.

(a) Process in Use at St. Joachimstal

St. Joachimstal in the Erzgebirge is the most important source of radium-bearing ores in Europe.   Here the process described below (2) has been applied continuously since 1910 under the control of the Austrian State.   Moreover, since the mines and factory were taken over by the Czecho-Slovakian authorities, nothing has been altered in the methods originally introduced.

The initial material is uranium pitchblende, the main constituent of which is U_3O_8, with admixture of very many other compounds, particularly PbS, SiO_2, CaO, FeO, and MgO.   It contains crystalline material in a highly dispersed state, the size of the individual crystals being only 10^{-4} to 10^{-7} cm. (3).   The broken-up ore is treated with sulphuric acid to which some nitric acid has been added, the concentration being such that the uranium goes completely into solution, whereas the radium remains behind quantitatively with the insoluble sulphates of calcium, barium and lead.   These are extensively worked up by heating three times in a solution of soda. The parts which still remain unaltered, the so-called " residual residues," contain amongst other things the whole of the tantalum, and we shall return to them in connection with the extraction of protactinium.   For the purpose of purification, the dissolved constituents are again precipitated as sulphate, converted into carbonates and then into chlorides.   Hereby the lead remains partly undissolved as chloride, and it is partly removed by means of a precipitation with sulphuretted hydrogen.   The final part of the process is the

fractional crystallisation of the mixture of radium and barium chlorides until the required concentration of the radium has been attained (4). Owing to its smaller solubility, the radium is concentrated in the crystals.

The quantity of radium produced per annum at St. Joachimstal only amounts to from 1 to 2 grams, owing to the difficulties to be overcome in the transport of the uranium ore.

(b) Process in Use at Denver

As a second illustration of the rational extraction of radium, we shall now describe the process developed in the years 1914 and 1915 at Denver, in the State of Colorado, North America (5). It deviates from the Austrian method mainly in consequence of the fact that the material to be worked up is carnotite, a vanadinate of potassium and uranium of composition $K_2O \cdot 2(U_2O.)V_2O_5 \cdot 3H_2O$. Moreover, the resources available for the equipment of the plant were much greater than in the previous case

The ore is treated with hot concentrated nitric acid, to which a small amount of hydrochloric acid has been added, and the whole of the radium is thereby brought into solution, in spite of the presence of sulphates. After partial neutralisation by means of NaOH, and addition of barium, it is then precipitated as sulphate together with barium and lead. The decanted solution is worked up for uranium and vanadium, whilst the sulphates obtained are mixed with wood charcoal in a graphite crucible, heated for 7 hours at 800° C, and so converted into sulphides. These are dissolved in hydrochloric acid, the lead removed by precipitation with hydrogen sulphide in ammoniated solution, whereas the barium and radium are precipitated as carbonate, and again dissolved in hydrobromic acid. The enrichment of the radium in the barium is in this case carried out by fractional crystallisation of the bromides.

The American carnotites contain on the average 4 mg. of radium per metric ton Up to the end of 1922 already 52,000 tons of the ore had been worked up, corresponding to the production of about 200 gm. of radium. In recent years, however, large quantities of still richer uranium ores have been found at Katanga (Belgian Congo), and at the present time the Belgian radium production monopolises the world's market

Mesothorium 1.—We shall proceed immediately with the description of the extraction of mesothorium, because, owing to its being

isotopic with radium, the extraction of the two substances is carried out by very similar processes. Mesothorium is to be found in every thorium mineral, there being $3 \cdot 10^{-10}$ gm. present with each gram of thorium. But since all thorium minerals also contain a small quantity of uranium, and 1 gm. of uranium corresponds to the presence of $3 \cdot 4 \cdot 10^{-7}$ gm. of radium, it follows that all mesothorium extracted from minerals must be mixed with an appreciable quantity by weight of radium, even though the amount of radiation from it may be much weaker. It can only be obtained as a " pure element " by awaiting its gradual regeneration in thorium salts. It can be isolated simply by precipitation with ammonia free from carbonates, eventually after the addition of a little barium, from which it can be separated again later by fractional crystallisation. But it is self-evident that, even after the lapse of years, only a very small yield by weight can be obtained in this manner. In its practical utilisation, the value of a mesothorium preparation is increased if it contains any of the longer lived element radium. The mesothorium content of radium is generally very small. If it has been derived from American carnotite, about $1 \cdot 5 \cdot 10^{-3}$ of the γ-radiation is due to mesothorium + radiothorium, whereas if it was obtained from Joachimstal pitchblende, this fraction only amounts to $6 \cdot 10^{-6}$.

The extraction of mesothorium on a large scale is carried out in conjunction with that of thorium. In the working up of monazite sand, a residue insoluble in sulphuric acid is obtained, and these insoluble sulphates are then worked up in exactly the same manner as that which has been described for the extraction of radium. If there is any doubt as to whether the initial material contains a sufficiency of barium, it is advisable to add a little of a barium salt.

Protactinium.—In the extraction of radium by the Joachimstal process it was mentioned that the "residual residues" were those parts of the initial material most difficult to bring into solution, and that in addition to acids of the rare earths they also contain protactinium, the higher homologue of tantalum. We obtain a fraction of similar composition by working up pitchblende with bi-sulphate of sodium. By treatment with hydrochloric acid the acids of the rare earths can be brought into solution, whereas barium and lead remain insoluble. On subsequently digesting with sulphuric acid we again obtain a deposit of tantalic acid, which can be freed from iron and other impurities by means of aqua regia. Another method consists in dissolving out the tantalum directly from the

pitchblende by means of hydrofluoric acid and sulphuric acid. In this process, the protactinium always remains with the tantalum, and we can thus obtain it without difficulty in a state of "radio-active purity," *i.e.* free from other radio-elements Since protactinium is not an isotope, but only a homologue of tantalum, there is every prospect that it will be possible to extract the small quantities —about $6 \cdot 7 . 10^{-8}$ gm per 1 gm. of uranium—of protactinium present in all uranium minerals, in a state of chemical purity, *i.e.* free from tantalum. It is of course always necessary, in the first place, to increase the tantalum content of the initial material by adding an arbitrary quantity, if we wish to achieve a quantitative yield. (Cf. the addition of barium in the extraction of radium and meso-thorium)

Actinium —This radio-element is a higher homologue of lanthanum, and it can be extracted together with this element from all uranium minerals, by means of the methods of separating rare earths (6) which are treated in detail in works of reference in chemistry. The concentration of the actinium as compared with the lanthanum salts is, however, met by similar difficulties to those which generally occur in the separation of rare earths from one another. But the difficulties are intensified on account of the fact that the radiological control of the concentration is very tedious, owing to the necessity for awaiting the development of disintegration products from the rayless * actinium. Hitherto it has been established that actinium is more strongly basic than lanthanum, and it is therefore only incompletely precipitated by ammonia, particularly in the presence of ammonium salts. A more convenient method of obtaining it will be rendered accessible when its parent protactinium has been prepared in weighable quantities in the chemically pure state , owing to the difference of their chemical properties, it will be a simple matter to separate the actinium from the protactinium

Ionium.—Up to the present we know of no uranium mineral that is absolutely free from ordinary thorium, and for this reason it has not yet been possible to prepare the isotopic element ionium in the pure state. But the mixed element obtained from uranium minerals practically free from thorium consists of equal parts of the two types

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* The β-radiation of actinium, the existence of which it is necessary to assume in order to explain its transformation into radioactinium (cf. p. 181 and p. 115), is too weak to be detected.

(7), and accordingly exhibits an appreciably smaller combining weight. Conversely, every thorium mineral contains appreciable quantities of uranium, from which slight traces of ionium are formed, and hence, although the atomic weight of the obtained thorium is not altered thereby, its activity is always more or less increased by the presence of this admixed ionium. For the separation of thorium-ionium salts from minerals, the methods that have been developed for ordinary thorium are, of course, applicable.

With reference to radiothorium, it has already been mentioned that it is always obtained together with thorium in minerals. It can be prepared as a pure element, if we start off with mesothorium in a state of radioactive purity. Radiothorium is regenerated gradually in the mesothorium, and after the lapse of a sufficient time a simple barium-thorium separation by means of NH_3 is carried out. Since the regenerated radiothorium is only present in unweighably small quantities, it is necessary to add, say, a ferric salt which forms a precipitate with ammonia, in order to obtain a visible precipitation. In this connection, reference may be made to the chemical treatment of the radio-elements of short life, described below.

Radium D —This is a constituent of radio-lead, which, although it is itself almost rayless, is responsible for the activity of several decades duration, inasmuch as it is the parent substance of radium E and polonium It can never be obtained in the pure state from minerals, for even though there may be no ordinary lead in the uranium mineral concerned, the latter inevitably contains radium G, which is likewise an isotope of lead. Moreover, as compared with the amount of RaG present, the amount of RaD is negligible in the quantitative sense. On the other hand, RaD can be obtained as a pure element from radium emanation, although the amount obtainable in this way is very small. But since this method belongs to those which can only be carried out in general with short-lived radio-elements, we shall defer the discussion of it till later. It is worthy of mention that the RaD associated with ordinary lead in the form of radio-lead is a very valuable material for radiologists, for it serves as a useful source from which radium E and polonium may be periodically obtained.

Polonium —This element can either be separated together with bismuth directly from uranium minerals, or it can be obtained more conveniently from radio-lead. As already mentioned, polonium is continuously being generated in this mixture of ordinary lead with

its isotopes RaD and RaG, until it is in equilibrium with the available RaD. Moreover, it is possible to obtain it in fairly concentrated form by recrystallising the radio-lead, preferably in the form of nitrate. The polonium remains in the mother liquor, and it may be finally obtained electrolytically and free from lead and radium B by maintaining a cathode potential that is not allowed to fall below $E_o = -0.08$ volt. In this connection, see also what is said about Radium A.* Gold or silver (8) is to be recommended in preference to platinum as the material of the electrodes, because the polonium cannot be redissolved quantitatively from the last named metal, owing to the formation of an alloy (9).

B. Preparation of the Radio-elements of Short Life

The shorter the life of the radio-element, the more it is necessary for the methods of preparing and purifying it to differ from the ordinary chemical ones, and the more it also becomes necessary to have recourse to measurements of activity, as a means of controlling these methods. In addition, the radio-elements of short life occur for the most part towards the end of the disintegration series, later on than the emanations. This circumstance also makes it advisable to describe them separately, for we shall see that the ease with which the emanations can be obtained in the pure state can also be utilised in the preparation of their succeeding products. For this reason, we shall first consider the methods of preparing the three emanations.

Being inert gases, the emanations are only occluded, and never chemically attached to the salts in which they are formed. They usually escape partially even at room temperature, whilst the major portion is liberated by heating, and if the salt concerned be fused, the whole of the emanation can be set free. By carrying out the fusion in a suitably designed apparatus, the whole of the emanation can be collected. Even at room temperatures the hydroxides and halides " emanate " best, whereas sulphates retain large quantities of the emanation. In order to collect radium emanation quanti-

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* Since it is rather troublesome to measure the individual potential of the electrode, we may make use of the following approximate instructions, which are quite satisfactory in practice. If the current be not allowed to exceed $3 \cdot 10^{-5}$ ampères per sq. cm. of the cathode surface, the nitric acid solution being of $\frac{1}{10} N$ strength, the polonium is extracted in a very pure state.

tatively, it is most convenient to dissolve the radium chloride or
bromide in water, to allow the sealed-up solution to stand until a
sufficient quantity of emanation has been generated, and then to
pump off the whole of the gases and transfer them to another vessel.
•By suitably constructing this vessel, we may use it to perform the
separation of the rare gases from the admixed gases nitrogen, oxygen,
hydrogen, ozone, etc., by the methods used in gas analysis.   The
oxygen, hydrogen, and ozone are always formed, in consequence of
the action of the radium rays on the water (see Chapter XXV).   It
often suffices to explode the explosive mixture of hydrogen and
oxygen, which constitutes the major portion of the mixed gases, by
sparking in a eudiometer tube similar to those used in gas analysis.
If it is required to obtain the emanation in still purer form, it is
advisable next to free the residual gases from carbon dioxide and
water vapour by contact with solid potassium hydroxide, and then
to condense the emanation by means of liquid air.   The uncondensed
impurities (nitrogen, hydrogen, rare gases) are then pumped off, and
after removal of the liquid air, the regasified emanation is allowed
to stream into the vessel in which it is to be used

It is obvious that such a detailed purification can only be carried
out with the relatively long-lived radium emanation ; in the case of
thorium and actinium emanations we have to content ourselves by
liberating and collecting them from the salts or solutions, even
though they are contaminated by large quantities of inactive gases.
They can never be utilised in the form of such intense sources of
radiation as radium emanation, but for most purposes, particularly
the extraction of their disintegration products, we are not disturbed
by the presence of the admixed inactive gases.

The first disintegration products of the emanations are the
" *short-lived active deposits*," this being the group name for the
products radium A, radium B, radium C, radium C' and radium C″,
and the corresponding disintegration products of the thorium and
actinium disintegration series   They are usually obtained by hanging
a negatively charged platinum foil in the vessel containing the
emanations.   The yield (*10*) is greater the larger the surface of the
platinum foil, and its negative charge only serves as a means of
concentrating the active deposit upon it.   The above-named
products are deposited on the foil, and can be obtained in solution by
means of dilute acids, and in large measure even with hot water.   If
necessary, they can then be separated.   In order to obtain thorium B

and thorium C, it is very convenient to use an apparatus like that depicted in Fig. 29 (p. 90). Situated at the bottom of this apparatus is a glass or platinum dish containing a salt of radiothorium or thorium X.

By a shorter or a longer exposure of the platinum foil in the emanation, we have a means of altering in a known manner the relative proportions of the A-, B- and C-products, so as to get a favourable yield of the substance desired. In this way, it is not difficult by means of very short exposures to obtain practically pure *radium A* (cf. p. 93). As a rule, however, it is necessary to effect a subsequent separation of the individual members of the active deposit. In the thorium and the actinium disintegration series, the A-products hardly call for consideration, owing to their very short life, and even radium A decays so rapidly that its removal does not present any difficulty, if we require only radium B plus radium C. It is sufficient if we wait about 20 minutes after the completion of the exposure in emanation before using the active deposit. We have just described the method of obtaining pure radium A, so that we need now only discuss the methods for the preparation of the *B*- and *C-products* in the pure form.

We can achieve a partial separation simply by heating the platinum foil ; thus at 800° C. 75 % of the thorium B volatilises and only 20 % of the thorium C. But the chemical and electro-chemical methods of separation are more effective.

In order to apply them, we first proceed to dissolve the active deposit from the platinum foil by means of dilute acids, and then make use of the known methods of separating bismuth and lead. Thus by means of electrolysis, if the cathode potential reaches the approximate value of $E_c = -0.5$ volt, but does not exceed this limit —which in a weakly acid solution corresponds to a current density of 0·4 milliamp. per sq. cm.—we can separate pure C, whereas the B remains almost entirely in solution. The separation of B can be almost completely prevented if we add to the solution a small quantity of isotopic lead in the form of a soluble lead salt, and so ensure that the very small quantity of lead that is separated out below the above-mentioned cathode potential, which is characteristic of lead in this state of dilution, consists almost wholly of inactive lead atoms. If the whole of the bismuth isotopes have been removed, the deposition of which already begins at a potential of $E_c = -0.08$ volt (corresponding to about 0·16 milliamp. per sq. cm.), it is sufficient

to increase the terminal voltage and produce a cathode potential exceeding -0.5 volt, when the B-products may now be separated out on an arbitrary electrode. If these are required, we should of course avoid previously adding appreciable quantities of inactive lead.

A still simpler method consists in dipping a clean sheet of nickel into the hydrochloric acid solution of B and C, instead of carrying out an electrolytic separation. As a result of a process which is essentially identical with that of electrolysis, the C-product is deposited free from the B-product on the nickel sheet (cf. p. 118).

It is never possible by means of acids to effect the quantitative solution of the radio-elements or of their oxides—for in air these are always present—from foils that have been activated in emanation. This is due to the occurrence of recoil and a diffusion of the radio-elements from the surface to the inside of the metal. When this diffusion, e g. that of polonium in gold (*11*), takes place very slowly, it is to be expected that the solution of the radio-element by means of acids will meet with success (see p. 166).

It should be emphasised that *radium E*, since it is isotopic with bismuth, can be obtained electro-chemically by the same methods as apply to the C-products, and that *radium A* and its isotope *polonium* are still more readily deposited, even at a cathode potential of $E_c = 0.35$ volt. In this case we can increase the degree of purity of the radium A or polonium by adding a salt of bismuth, when the deposition of the radium C or radium E along with the radium A or polonium is rendered impossible. For the electro-chemical separation of polonium and radium E, radio-lead from minerals is not the only source from which they may be derived. We may also use the " active deposit of long life," which is formed when we allow radium emanation to decay in a closed vessel. Under such circumstances, the *radium D* is situated on the walls of the vessel, and can be dissolved by means of acids. Radium E and radium F are constantly being regenerated in this solution, and owing to their concentration they can be obtained more conveniently from it by the above described electro-chemical processes than from radio-lead, which is only soluble in larger quantities of liquid. Non-noble radio-elements, such as the isotopes of thorium, radium, and actinium, can also be deposited electrolytically when in the form of hydroxide or carbonate, by using high current densities (*12*).

Short-lived thorium isotopes like *uranium X, radiothorium*, etc., can be deposited electro-chemically on platinum wires from a hydrochloric acid solution, with a yield of about 60 % (*13*).

For radio-elements to which they can be applied, the electro-chemical methods of separation are generally preferable to all others, chiefly owing to the fact that the substances are in this way obtained not only in a state of radio-chemical purity, but also in a state of chemical purity.

Another very elegant method of separation is based on the utilisation of the phenomenon of "*radioactive recoil*" (see Chapter VI), but its range of applicability is still more restricted. We may conveniently obtain the thallium isotopes *thorium C″* and *actinium C″* when they recoil in air from a metal plate coated with the active deposit. They are collected on a negatively charged metal plate placed opposite to the activated plate. We may also derive pure *radium B* in this way by the recoil from radium A, but in this case we must terminate the experiment after a duration of a few seconds, for otherwise the radium B collected will already be mixed with the radium C that has been generated from it.

In conclusion, we must deal with those methods of preparing and separating short-lived radio-elements which are most generally applicable, namely, the *chemical methods*. We have accurate information as to the chemical nature of all the radio-elements of short life. We know that we are dealing with different types of thallium, lead, bismuth, and polonium (these are the products A to G), and further, that thorium X (*14*) and actinium X are isotopes of radium , uranium X_1, uranium Y, and radioactinium are isotopes of thorium, and that mesothorium 2 is chemically identical with actinium, and uranium X_2 with protactinium. The analytical chemistry of these substances must always be attended with difficulty inasmuch as they are always present only in exceedingly small concentration. This will be clear if we recall that in ordinary radio-chemical work a content of 10^{-11} mol of thorium B per litre would be pronounced a fairly " strong " solution. An artifice which must always be successful in overcoming the difficulties attendant upon the extreme dilution of these substances consists in the addition of an isotope in weighable quantities. Thus, if we wish to remove thorium B quantitatively from a solution, it suffices to add a little lead nitrate, and to precipitate the entire lead by means of sulphuretted hydrogen. All the atoms of the mixed element lead so obtained, and consisting of ordinary lead and

thorium B, are chemically identical, and hence, by passing sulphuretted hydrogen through the solution, the thorium B must have been removed to the same degree of completeness as the practically insoluble lead sulphide.

A disadvantage of this method consists in the fact that once such mixing has been carried out, the process is practically irreversible, and hence the radio-element can never again be obtained in concentrated form. For this reason we should only make use of this method of adding an isotope when we are concerned with the quantitative removal and not with the preparation of a radio-element. In the latter case, it is always advisable not to use an isotope, but to have recourse to a related element as a carrier in the precipitation reaction. This is analogous to the addition of barium in the extraction of radium or mesothorium, already discussed, for we can in this way effect a separation from the more distant elements, and still bring about the final separation of the radio-element from the barium added. Correspondingly, it is often better to precipitate, say, radium E by the admixture of lead rather than of bismuth, for in this way it can easily be separated again by electro-chemical means (see above). Likewise, we should make use of zirconium or cerium rather than thorium for the separation of uranium X_1, and so on.

When a related element and not an isotope is used, we can no longer maintain that the radio-element must also be removed by every quantitative precipitation of this substance. Lead sulphate, for instance, would leave the radium E in solution, whereas lead sulphide would remove it quantitatively. In such cases, the adsorption and precipitation rule which we have already discussed (p. 120) is applicable. A radio-element will be adsorbed and precipitated by those deposits the anions of which form with the radio-element concerned a compound which has a low solubility in the solvent available. In the place of the isotope, we should thus be able to use any other element for mixing purposes, provided that, like the radio-element, it forms an insoluble precipitate with the anion in the solution. Instead of the hydroxide precipitation of the thorium isotopes we may utilise the hydroxide precipitation of iron salts, or in place of the sulphate precipitation of the lead isotopes we may bring about the sulphate precipitation of barium salts, etc.

It is sufficient for us simply to direct attention to these rules here, since they have done invaluable service in the domain of

the analytical chemistry of the radio-elements, if we disregard one or two results which have not yet been entirely explained, but which are probably only apparent exceptions to the rules.   Our knowledge of them places us in the position of being able to give a clear summary of the methods of separation of the radio-elements of short life which have been tested hitherto, and to predict new and suitable methods   It must be left to the analytical experience of the chemist to decide which individual process is to be recommended, according to the special problem on hand.

THE PROPERTIES OF THE INDIVIDUAL
RADIO-ELEMENTS

In this chapter we shall discuss the individual radio-elements in the order of their production from the parent substances uranium, protactinium and thorium, and in each case we shall give the most important data which serve to characterise that radio-element from the physical and chemical points of view   It will suffice if we are brief here, because in the preceding and more general chapters we have also frequently made reference to the special properties of the radio-elements   Thus we shall only deal with the methods of preparation in so far as in one case or another the systematic treatment given in Chapter XXIII requires to be supplemented from the practical viewpoint   In conclusion, we shall devote a few words to the radioactive elements potassium and rubidium, which stand in an isolated position as compared with the rest of the radio-elements, and which have not even now been very thoroughly investigated.

The significance of the letters used for brevity is as follows :

Z = Atomic number ;

A.W. = Atomic weight ,

T = Half-value period ,

R = Range in cm. in air at 760 mm pressure and 15° C. ,

μ = Coefficient of absorption in aluminium, measured in cm.$^{-1}$.

A The Uranium Series
1. *Uranium*

Uranium is a mixture of two isotopes, uranium I and uranium II.

	Uranium I	Uranium II
Z	92	92
A W	238·18	234
T	5 10^9 years	2 10^6 years
Radiation - - -	a	a
R (1) - - - -	2·83	2·91
Parent element - -	—	UX$_2$
Daughter element - .	UX$_1$	Io

Since the period of life of uranium II is much shorter than that of uranium I, the mixed element "uranium" only contains 0·04 % of uranium II, and can therefore be regarded from the chemical point of view as being pure uranium I. The combining weight determined experimentally has the value 238·18. The fact that this is in excess of an integral value 238 is possibly due to the presence of a third, as yet undetected isotope of atomic weight higher than 238 (see under protactinium). As far as we know at present, uranium is the element of highest atomic number and of highest combining weight. We shall not enter into its chemical properties here, as they are to be found in every text-book of chemistry. In radioactive investigations we generally use the black oxide of uranium (U_3O_8), or the yellowish fluorescent uranyl nitrate—$UO_2(NO_3)_2 . 6H_2O$—the former as a standard for a-ray measurements and the latter for the preparation of uranium X   For information as to the occurrence of uranium minerals and the methods of extracting radium from them, reference should be made to pp. 160 to 162.

The a-activity of uranium in equilibrium with all its transformation products is 4 73 times as large as that of the uranium itself (2).

2. Uranium X_1 and Uranium X_2

	Uranium X_1	Uranium X_2	
Z - - - - -	90 (=thorium)	91 (=protactinium)	
A.W. - - - -	234	234	
T - - - -	23·8 days	1·175 minutes (3)	
Radiation - - -	β	β, γ	
μ - - - -	510	β 14 4	γ 24 0 70 0·14
Parent element - -	U I	UX_1	
Daughter element - -	UX_2	U II	

Uranium X_1 is an isotope of thorium (see Table XXIII, p. 112); it can thus be most conveniently separated from solutions of uranium salts by precipitation with iron or zirconium hydroxide (see p. 171). Uranium X_2, an isotope of protactinium, is obtained from solutions of uranium X_1, by electrolysis, or by joint precipitation with tantalum oxide.

3. Uranium Y and Uranium Z

The genesis of these two products, both of which are found in uranium salts, has not yet been entirely explained. Uranium Y

$(T=27\cdot8$ hours) (3) is an isotope of thorium, and uranium Z $(T=6\cdot7$ hours) is an isotope of protactinium (4). Both are β-rayers $(\mu_{UY}$ ca. 300, μ_{UZ} ca. 100), and it follows from the smallness of their contribution to the total activity of uranium salts that they cannot occupy a place in the main disintegration series. Uranium Y is most probably the parent of protactinium, and hence of the actinium series (cf. Table XVII, p. 101). On the other hand, uranium Z is a daughter element of uranium X_1, which suffers dual disintegration. The beginning of the uranium-radium disintegration series is therefore representable schematically (5) in the following way :

$$
\begin{array}{c}
U_I \\
\alpha \downarrow \\
UX_1 \\
\end{array}
$$

$$99\ 65\ \% \quad \beta \swarrow \qquad \beta \searrow \quad 0\ 35\ \%$$

$$UX_2 \qquad\qquad UZ$$

$$\beta \qquad\qquad\qquad \beta$$

$$\searrow U_{II} \swarrow$$

$$\alpha \downarrow$$
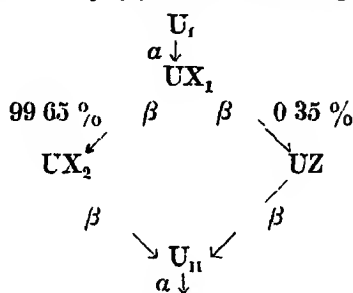
4. *Ionium and Radium*

				Ionium	Radium
Z	.	.	.	90 (=thorium)	88
A W.	.	.	.	230	226
T	.	.	.	10^5 years (6)	1580 years *
Radiation	-	-	-	$\alpha\ (\gamma)$	$\alpha\ (\beta)\ (\gamma)$
R	.	.	.	3·194	3·389
Parent	-	-	-	U_{II}	Io
Daughter	-	-	-	Ra	RaEm

Ionium, an isotope of thorium, has not yet been prepared in the pure state. We are familiar with a thorium preparation relatively rich (7) in ionium (cf. however, p. 164), of which it contains 30 % and yielded a combining weight of 231·51 (A.W. of ionium $=230$, of thorium $=232\cdot12$).

* The half-value period of radium is fundamental in connection with the constants of its long-lived " fore-parents " It is found either by counting the number of α-particles emitted by a known amount of radium, or by measuring the growth of radium from ionium. The former method has yielded values lying between 1580 and 1730 years, and the latter, values between 1660 and 1690 years.

We have already described the processes used in the preparation of radium.   It is generally brought into the market in the form of the chloride or bromide, mixed with the corresponding salt of barium. The international radium standard is kept in Paris and consists of 21.99 mg. of anhydrous $RaCl_2$; the secondary international radium standard is kept in the Radium Institute of Vienna, and contains 31.17 mg. of anhydrous $RaCl_2$.   Both standards are composed of the purest $RaCl_2$, free from every trace of barium.   The price of radium preparations is determined by their content of the element radium ; in the autumn of 1923 the general market price of 1 mg. radium was about 70 dollars.

The fact that radium, in spite of its rarity, has already been prepared in quantities of the order of a few hundreds of grams, removes the difficulty of determining the properties (8) of this element by the usual methods in general use in chemistry and physics.   The evidence adduced from its spectrum, the solubility of its salts, etc., all showed it to be a higher homologue of barium.   Thus the solubility of its sulphate is smaller than that of any of the other sulphates of the alkaline earths, as is shown in Table XXX.

TABLE XXX

Solubility of the Sulphates of the Alkaline Earths

	Solubility at $25°$ C in per cent. by Weight (Grams of the Substance in 100 gm of the Solution)
$CaSO_4$	$2.1 \quad 10^{-1}$
$SrSO_4$	$1.5 \quad 10^{-2}$
$BaSO_4$	$2.3 \quad 10^{-4}$
$RaSO_4$	$2.1 \quad 10^{-6}$

For the most part, we have access to salts of radium in quantities of only a few milligrams, and mixed with barium.   In such cases it is most convenient to determine them quantitatively by the measurement of their radioactivity.   In contrast to the method of weighing, the degree of purity of the radium salt is without significance in estimations by this method.   We must, however, compare the unknown preparation with a radium salt of known radium content, which has been standardised directly or indirectly by means of the International Standard.   When the intensity of the γ-rays is used as the basis of the measurement, the method has a further advantage

in that the preparation can remain in a sealed-off glass tube,* which is the usual mode of packing. Very weak preparations must be brought into solution, and the most accurate method of estimating them is by the measurement of the emanation. In this method, when the emanation is in equilibrium with the amount of radium present, it is driven into an electroscope that has been previously calibrated by known quantities of emanation.†

A weak β-radiation from radium is also mentioned in the Table. This does not originate in the nucleus—otherwise an isotope of actinium would be detectable as a disintegration product—but is of secondary origin, being released from the K- and L-levels by γ-rays (cf. p. 73). The value of the coefficient of absorption is $\mu = 312$ cm.$^{-1}$. The γ-radiation proper to radium only amounts to approximately 1 % of the total γ-radiation emitted by a radium preparation which is in equilibrium with its disintegration products. The α-activity of radium, exclusive of that of its disintegration products, is 0·60 times the α-activity of uranium, which of course always contains the two α-rayers, uranium I and uranium II (cf. Table XIX, p. 103).

5. Radium Emanation

Z	86
A W. . . .	222
T	3·810 days (10)
Radiation . .	α
R	4·122
Parent . . .	Ra
Daughter . . .	RaA

Radium emanation is the highest homologue of the rare inert gases. Owing to its inability to enter into chemical reactions, and from the nature of its spectrum (11), it was possible, at an early stage, to allot it a corresponding place in the periodic classification. Later on, sufficiently large quantities of it were obtained for the determination of some other of its constants. Its boiling point is situated

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* It has been suggested that the unit of measurement for such γ-ray measurements should be called an "Eve." This is the intensity of the γ-radiation from 1 gm. of radium at a distance of 1 cm from the source of the radiation (9)

† For information on the practical aspects of the methods of measurement, the works mentioned in the Preface may be consulted.

at $-62°$ C., its freezing point at $-71°$ C., and its critical temperature at $105°$ C.   At room temperature, the emanation is distributed in the proportion of $1 : 3$ between water and an equal volume of air in a closed vessel, so that its distribution coefficient (a) has the value 0.3. With rising temperature, the solubility decreases in strict accordance with Henry's law, as shown in Table XXXI.   The solubility is also diminished by the addition of salts to the water ; thus for uni-molar salt solutions the value of a is about 0.16.   The distribution coefficient between blood and air amounts to 0.42 at body temperature.

TABLE XXXI

Distribution of the Emanation between Water and Air

Temperature in °C	Distribution Coefficient (a) between Water and Air
0	0·510
10	0·350
20	0·255
30	0·200
40	0·160
50	0 140
60	0 127
70	0 118
80	0 112
90	0·109
100	0·107

Organic liquids dissolve very much more emanation than water ; thus for acetone ($a=6.3$), petroleum ($a=10$), hexane ($a=17$), olive oil ($a=28$), etc. (*12*).   The velocity of diffusion of emanation in water amounts to 0.82 cm ^{2}/day at $14°$ C.   Furthermore, solid bodies like rubber, paraffin wax, platinum black, and particularly charcoal (*13*) adsorb the emanation very strongly.   Under certain circumstances radium preparations occlude an appreciable fraction of the emanation produced in them.   Salts which emanate badly in this way can be improved by moistening, pulverising, or by transforming them into the hydroxide or halide (*14*).

The volume of emanation in equilibrium with 1 gm. of radium is 0.63 mm.^{3} ($=6 . 10^{-6}$ gm.).   This quantity of emanation is called 1 " Curie " ;   both it and its thousandth part (" Milli-Curie ") are used as units of measurement for quantities of emanation.   A unit of measurement for concentrations of emanation is called a " Mache " ;

thus, spring water has an emanation content of 1 Mache when the quantity of emanation in 1 litre of this water would produce a saturation current of $1 . 10^{-3}$ electrostatic units, if it were transferred to an electroscope and if its radiation in all directions were utilised (15). One Mache unit is equal to $3.6 . 10^{-10}$ Curie per litre.* The emanation content of strongly radioactive springs often amounts to several thousand Mache units (cf. p. 220). Examples are given in Table XXXII.

TABLE XXXII

Emanation Content of Several Springs, expressed in Mache Units

Oberschlema - - ca 3000	Ischia (Old Roman Spring) -	370
Joachimstal (Water in mine) 2050	Gastein (Grabenbäcker Spring)	155
Brambach (Wettin Spring) - 2000	Aix les Bains (Alum Spring) -	56
Joachimstal (Spring Head) - 600	Karlsbad (Muhlbrunnen) -	32

6. *The Short-lived Active Deposit of Radium*
(RaA, RaB, RaC, RaC′, RaC″)

	RaA	RaB.	RaC	RaC′	RaC″
Z - -	84 (=polonium)	82 (=lead)	83 (=bismuth)	84 (=polonium)	81 (=thallium)
A.W - -	218	214	214	214	210
T - -	3·05 min	26·8 min	19·5 min.	10^{-6} sec. (16)	1·38 min.
Radiation -	α	β, γ	α, β, γ	α	β
R - -	4·722		α 3·8	6 971	
μ - -		β 890 γ 230 / 80 40 / 13 0 57	β 53 γ 40 / 13 0·230 / 0·127		
Parent -	RaEm	RaA	RaB	RaC	RaC
Daughter -	RaB	RaC	99·97% RaC′ 0·03% RaC″	RaD	RaD (?)

The first five disintegration products of the gaseous radium emanation are isotopes of the metals polonium (17), lead, bismuth, or thallium, and since they are solids, they have the tendency to be

* Recently a new unit for the measurement of concentrations of emanation has been suggested . 1 " Eman " $= 10^{-10}$ Curie/litre.

deposited as soon as they are produced. Moreover, with the exception of a very small fraction they are positively charged, and hence they are deposited most easily on negatively charged surfaces. This fact is made use of in their preparation (cf. p. 60). In consequence of their rapid transformation, most of our observations are made with mixtures of them, and we have already described the resulting complicated decay curves (p. 93). The short-lived active deposit of radium also emits an exceedingly small number of α-particles of ranges 9·3 and 11·2 cm. (*18*)

7. *The Long-lived Active Deposit of Radium*

(RaD, RaE, RaF or Polonium)

	RaD.	RaE.	RaF.
Z - -	82 (=lead)	83 (=bismuth)	84 (=polonium)
A.W. - -	210	210	210
T - - -	16 to 20 years	4·85 days (*19*)	136 days (*20*)
Radiation -	β, γ	β, γ	α
R (*21*) - -			3·925
μ - - -	β 5500 | γ 45 | 0·99	β 43 | γ 0·24	
Parent - -	RaC′	RaD	RaE
Daughter -	RaE	RaF	RaG

The activity of a metallic surface coated with the short-lived active deposit of radium does not fall to zero, but manifests a very weak residual radiation (β-rays of RaD), to which are gradually added later new β- and α-rays (RaE and RaF). (See p. 93 for the curves of activity.) Not until the RaF has disintegrated does the whole of the activity disappear. The resulting end-product of the uranium-radium series does not emit rays, and is hence stable. According to the group displacement laws this end-product must be an isotope of lead, and it has been found in the pure state as " lead of atomic weight 206 " in crystalline uranium minerals.

Radium D is also an isotope of lead, but owing to the presence of other types of lead in them, it cannot be obtained in the pure state from minerals. But it has been separated in quantities just visible and in the pure state from vessels in which about 1 Curie of emanation has been allowed to decay (cf. pp. 157 and 169) ; its electro-chemical properties corresponded exactly to those of ordinary lead.

Radium E is an isotope of bismuth. In view of its short period of life, it would appear to be impossible to obtain it in visible quantities.

Radium F or polonium is the most important representative of the element of atomic number 84; the other types of this element, the " A "- and " C' "-products, are still much more unstable. The chemical properties of this otherwise unknown element have therefore to be studied with radium F, and are in part already very well known. It resembles very strongly its atomic analogues, bismuth (22) and tellurium, as is shown by the whole of its behaviour in analytical chemistry, by its electro-chemical potential—which lies near to that of silver—and by its ability to form a gaseous compound with hydrogen. Like tellurium hydride, polonium hydride decomposes in the moist state in a few minutes (23). As already mentioned (p. 121), polonium occurs in the colloidal state in neutral or in weakly acid solutions.

B. THE ACTINIUM SERIES
1. *Protactinium and Actinium*

	Protactinium	Actinium
Z	91	89
T	ca 10,000 years (24)	ca. 20 years
Radiation . .	a	β
R	3·67	
μ	—	Unknown
Parent . . .	UY (?)	Protactinium
Daughter . .	Actinium	Radioactinium

It is seen from the above Table that uranium Y is presumed to be the parent of protactinium; this is due to the fact that this arrangement fits in well with the displacement laws, and with the branching ratio of the actinium series (see Chapter X). It has not yet been possible to obtain direct proof of the genetic relation between UY and Pa. Moreover, the identity of the parent of the short-lived UY is still quite uncertain. We can only say that it is most probably a type of uranium, since the actinium series (25) is present in a constant proportion (3 % of the activity) in all uranium minerals. It still remains an open question as to whether the branching of UY takes place at uranium II, as assumed in Table XVII [(p. 101), or at uranium I. A third possibility is that

there may exist an element uranium III (26), hitherto undetected, and from which only the actinium series is derived, whereas U I and U II pass over completely into the radium series. This also renders it impossible to calculate the atomic weight of any member of the actinium series. Moreover, since as yet no member of the actinium series has been prepared pure in sufficient quantity to enable its atomic weight to be determined experimentally, we are deprived of any certain method of evaluating this important constant for the whole series. If we assume the scheme given in Table XVII to be correct, the atomic weight of protactinium would be 230, that of actinium 226, etc. But we have hopes that it will be possible to obtain pure protactinium before long (see p. 164), and the determination of its atomic weight would at the same time clear up the question of the parent substance

The chemical properties of protactinium (27) are exactly those to be expected of a higher homologue of tantalum (see p. 163), and hence its separation from tantalum is correspondingly difficult. Actinium is a higher homologue of lanthanum, and since it is a new element, it would be interesting if it could be prepared in the pure form. Attempts have been made, but hitherto without success; and owing to the short life of the element it is doubtful whether weighable quantities will be obtainable.

2. *Radioactinium, Actinium X and Actinium Emanation*

	RdAc	AcX.	AcEm.
Z - - -	90 (= thorium)	88 (= radium)	86 (= emanation)
T - - -	18·9 days	11·2 days	3 92 secs.
Radiation -	α, β, γ	α	α
R - - -	α 4·61	4 26	5·57
μ - - -	β | γ 175 |25 , 0 19		
Parent - -	Ac	RdAc	AcX
Daughter -	AcX	AcEm	AcA

Special attention is merited by one rather striking feature expressed in the above Table. AcX emits α-rays of smaller velocity than RdAc, which has a longer period of life; this constitutes a breach of the general rule relating to the connection between period of life and range (p. 106).

As with Ra and RdTh, the β-rays of RdAc may be assumed to be of secondary origin.

For the chemical separation of RdAc from Ac and simultaneously from AcX, we utilise the fact that thorium is readily precipitated in weakly acid solution by means of thio-sulphate or hydrogen peroxide (*28*). In order to obtain a visible deposit, we may add a trace of a thorium salt, or still better of a salt of the non-isotopic element zirconium (cf. Chap. XXIII, p. 171) before the precipitation. In this way we obtain AcX together with Ac in the filtrate, and it may be freed from Ac by repeated precipitation with ammonia solution. Of course, we must add a little iron or similar element before each precipitation with ammonia, in order that a deposit may be obtained, the anions (OH'-groups) of which then act as carriers for the Ac (cf. the rule on p. 119). We may obtain AcX in a very pure form by means of recoil from solid preparations of RdAc (cf. p. 170).

Like radium emanation, actinium emanation is a rare inert gas, the physical constants of which (velocity of diffusion (*29*), solubility, etc.) have not been determined with any very great accuracy, owing to its extremely short period of life (*30*) and the correspondingly small quantities of it available In view of the isotopy of the two emanations, however, we may assume the properties of AcEm to be identical with those of RaEm.

3 The Active Deposit of Actinium
(AcA, AcB, AcC, AcC', AcC″)

	AcA	AcB.	AcC	AcC'	AcC″.
Z - -	84 (= polonium)	82 (= lead)	83 (= bismuth)	84 (= polonium)	81 (= thallium)
T - -	2 . 10⁻³ sec	36·1 min.	2·16 min	ca 5 . 10⁻³ sec.	4·76 min.
Radiation	α	β, γ	α, β	α	β, γ
R - -	6 27	—	α 5·15	6·4	—
μ - -	—	β large | γ 120 / 31 / 0·45	—	—	β 28·5 | γ 0·198
Parent -	AcEm	AcA	AcB	AcC	AcC
Daughter	AcB	AcC	0·16% AcC' 99·84% AcC″	AcD (?)	AcD

A comparison with the Table on p. 179 reveals immediately the great similarity between the individual members of the active deposit of actinium and the corresponding members of the short-lived active deposit of radium as regards their sequence and radiation. Apart from the different numerical values of T, R and μ, the following important differences exist. In the first place, with AcC the majority of the atoms disintegrate with emission of a-radiation into AcC″, whereas in the case of RaC practically all the atoms are transformed into RaC′ with emission of β-rays ; secondly, AcD is already the stable end-product of the series, whereas RaD, although it is much more stable than the previous members of the series, still possesses the character of a radio-element, and introduces us to the "long-lived active deposit" of radium, which has no analogue in the actinium series

C THE THORIUM SERIES

1. *Thorium, Mesothorium 1, and Mesothorium 2*

	Thorium	Mesothorium 1.	Mesothorium 2
Z · · ·	90	88 (=radium)	89 (=actinium)
A.W · ·	232·12	228	228
T · · ·	$2 \cdot 2 \cdot 10^{10}$ years	6·7 years	5·95 hours (*31*)
Radiation ·	a	(β)	β, γ
R · · ·	2 72	—	—
μ · · ·	—	—	β 40-20 $\mid$ γ 26 0·116
Parent · ·	—	Thorium	Mesothorium 1
Daughter ·	Mesothorium 1	Mesothorium 2	Radiothorium

The element thorium is the parent element of a radioactive series which seems to be completely independent of the uranium-radium and the actinium disintegration series. This is evidenced by the fact that the contributions of the two series towards the activity of various minerals fluctuate within wide limits. We are familiar with uranium minerals that are practically free from thorium and its decay products, and conversely, there are thorium minerals containing very little uranium, and hence also very small quantities of ionium and radium. The main source of thorium is monazite sand, containing about 4-5 % of ThO_2. A few rare minerals are much richer in thorium, such as the thorianite found in Ceylon, which sometimes

contains as much as 70 % of ThO_2. The chemical text-books contain information upon the preparation of pure thorium. In radioactive investigations it is generally used in the form of nitrate or hydroxide ; the former, for instance, when we require a soluble salt for the purpose of separating out ThX, and the latter for the collection of thorium emanation, owing to the fact that it " emanates" freely.

We have already spoken (Chapter XXIII, p 162) about the preparation of *mesothorium*, and of the impossibility of obtaining it completely free from radium. We can determine the approximate radium content of mesothorium preparations on the market without opening them, by absorption measurements of the γ-rays for various thicknesses of the absorbing sheets (see p. 48). More reliable values are obtained by determining the amount of radium emanation produced in them (*32*).

We are unable to detect the rays emitted by mesothorium 1, but from the fact that the succeeding product mesothorium 2 has an
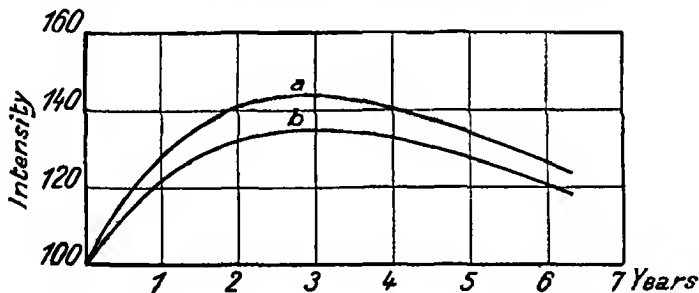
FIG 37   Variation of the γ-Activity of Mesothorium with Time

atomic number 89, we must conclude that each atom loses a β-particle when it is transformed into mesothorium 2. The activity is due exclusively to the radiation from the disintegration products, particularly that of mesothorium 2, which, owing to its short half-value period, is present practically in its equilibrium amount even after a period of three days. An appreciable quantity of radiothorium will be present in older preparations of mesothorium, since the half-value period of RdTh is only 1·9 years (*33*). In consequence of this, we have to take account of the additional very penetrating γ-radiation from ThC". Fig. 37 indicates the manner in which the resulting total activity of a " mesothorium preparation " alters in the course of years (*34*). Curve *a* was obtained with freshly prepared

mesothorium, free from radium, whilst curve b was obtained with a new preparation of mesothorium, containing radium (cf. footnote on p. 48). In these measurements, the rays were passed through lead of thickness 3·3 mm. In both cases, the maximum intensity was attained after a period of about 3 years, but the increase was greater for the preparation free from radium than for that containing radium. In the former case the activity rose from 100 to 143·8, the increase amounting to about 44%, whereas in the latter case the activity rose from 100 to 135, or by only 35% If the measurements had been performed after passage of the rays through 5 mm. of lead, instead of through 3·3 mm., the form of the curves would have been essentially the same, but the rise would have been slightly more pronounced for the mesothorium containing radium, owing to the fact that the γ-radiation from radium relative to that from mesothorium would be somewhat less effective after passing through 5 mm. of lead, than after passing through 3 mm.

The amount of MsTh available by weight is always extremely small, for 3 3 . 10^9 gm. of thorium are required to produce an equilibrium amount of 1 gm. of $MsTh_1$. On the other hand, the activity of 1 gm. of radium is equivalent to about $\frac{1}{540}$ of the same quantity of mesothorium, and hence to as much as would be in equilibrium with about 1·4 . 10^7 gm. of thorium (35)

2. *Radiothorium, Thorium X, and Thorium Emanation*

	Radiothorium.	Thorium X.	Thorium Emanation.
Z - - -	90 (= thorium)	88 (= radium)	86 (= RaEm)
A.W. - -	228	224	220
T - -	1 90 years	3·64 days	54·5 seconds
Radiation -	a, β	a	a
R - - -	a	4 30	5·00
	3 87		
μ - - -	β		ϵ
	large		
Parent - -	Mesothorium 2	Radiothorium	Thorium X
Daughter -	Thorium X	Thorium Emanation	Thorium A

The β-rays of RdTh do not originate in the nucleus, but are of secondary origin, like those of radium and RdAc. They are probably released from the L- and M-levels by a γ-radiation, which has not yet been detected directly.

We have already mentioned the method of preparing radio-thorium in Chapter XXIII. ThX may be periodically obtained from a preparation of RdTh, by precipitating the latter together with iron, aluminium or similar element by means of ammonia, when the ThX remains in the filtrate (cf. the method above described for the preparation of the isotopic AcX). Radiothorium and thorium X are chiefly used as sources of thorium emanation and its short-lived disintegration products. It is advisable to maintain preparations that have been made for this purpose permanently in a moist condition, because they then part with their contained emanation much more readily.

3. *The Active Deposit of Thorium*
(ThA, ThB, ThC, ThC', ThC")

Comparisons of the accompanying Table with that for the active deposit of actinium and with that of the short-lived active deposit of radium (p. 183 and p. 179) reveal the great similarity between these sections of the three disintegration series. Characteristic of

	ThA	ThB	ThC	ThC'.	ThC".
Z . .	84 (=polonium)	82 (=lead)	83 (=bismuth)	84 (=polonium)	81 (=thallium)
A W .	216	212	212	212	208
T . .	0·14 sec.	10·6 hour	60·8 min.	ca 10^{-11} sec	3·20 min.
Radiation	α	β, γ	α, β	α	β, γ
R . .	5·70	—	α 4·80	8·60	—
μ . .	—	β 153 $\mid$ γ 160, 32, 0 36	β 14·4	—	β 21·6 $\mid$ γ 0·096
Parent -	ThEm	ThA	ThB	ThC	ThC
Daughter	ThB	ThC	65% ThC' 35% ThC"	ThD	ThD

thorium is the branching ratio of the C-product. In this case comparable quantities disintegrate with the emission of α- and of β-rays respectively, whereas with AcC practically the whole takes the first course, and with RaC the main disintegration is attended by the emission of β-rays. According to the displacement laws it is to be expected that the two branch series will lead to the

same end-product, the lead isotope ThD, and in point of fact a type of lead with almost the atomic weight calculated for ThD has been found in thorium minerals (cf. p. 111) (*36*).   It has not yet been definitely proved whether both the types of lead,—produced in the proportion by weight of 35 : 65—are stable, or whether one of them is transformed into an isotope of bismuth with accompanying emission of β-rays (cf. p. 134, footnote).

Althouth the A-product is of longer life than in the case of the actinium series, it is just as impossible to separate it from the emanation.   Both products reveal themselves by the fact that we observe the scintillations produced by the emanations to occur always in pairs.   In the case of actinium (T for AcA $= 2$. 10^{-3} sec.) the two members of such a pair of scintillations appear simultaneously, whereas in the case of thorium (T for ThA $= 0$ 14 sec.) we perceive a distinct interval between the two scintillations, albeit a very short one.

ThB and ThC are particularly suitable for use as indicators in physical and in chemical investigations, and have often been used for this purpose (cf. Chapter XV).   This is due to the fact that they are easily prepared and their half-value periods (*37*) are so different that we can conveniently determine them quantitatively, one along with the other.

The active deposit of thorium also emits α-particles of range 11·5 cm.   For every 10^{6} α-particles of range 8 60 cm. (ThC′) there are 220 of these particles of long range (*38*)

D. Potassium and Rubidium

From amongst the numerous chemical elements, it has been found by very careful measurements that two, apart from uranium and thorium, emit a constant but only very weak radiation.   These elements are potassium ($Z = 19$; A W. $= 39$ 10), and rubidium (*39*) ($Z = 37$; A.W. $= 85·5$).   Both are β-rayers, and although the rays emitted by potassium are the more penetrating, the number of β-particles ejected from equal quantities by weight is greater in the case of rubidium.   For rubidium, μ has been found to be 347 ; the intensity of its radiation is therefore reduced to half its initial value by a sheet of aluminium 0·020 mm. thick, and its rays are thus somewhat harder than those of UX_1.   In the case of potassium, two different absorption coefficients are found, namely, $\mu = 28$ and $\mu = $ ca. 70.   The harder rays from potassium are therefore about 12

times more penetrating than those from rubidium ; their velocity attains to 88 % of the velocity of light, whereas that of the rays from rubidium only reaches about 60 % c.

Since, as already mentioned, the β-rays of rubidium have almost the same penetrating power as those of UX_1, the ratio of the activities of equal parts by weight of uranium and rubidium supplies us with information as to the effective activity of rubidium, provided we only measure the β-rays of UX_1, and not say those of UX_2, or still less the α-rays of uranium.   The ratio is found to be 15 : 1, so that rubidium is 15 times less active than an equal weight of uranium. If the β-rays originate in one of the two known isotopes of rubidium (A.W. $=85$ and 87), and not in eventual admixed small quantities of an active isotope as yet unknown, we can calculate the half-value period of rubidium, and find it to be about $7 . 10^{10}$ years.   An indefinitely thin layer of potassium is roughly 10 times less active than the same weight of rubidium in similar form, so that in this case, if it is the isotope of A.W $=39$ that emits the β-rays, we can estimate that the half-value period of potassium has a value 10 times as large as that of rubidium.

Since the β-radiation of rubidium is itself distinctly softer than that of potassium, we may perhaps conclude that an eventual β-radiation from caesium might have escaped detection, in conquence of its still greater softness.   It has been established, however, that the total ionisation which might be produced by caesium (inclusive of eventual α-rays) has a value less than $\frac{1}{70}$ that of rubidium, the corresponding eventual total ionisation from sodium also being less than $\frac{1}{50}$ that from potassium (40)

By careful experiments it has been shown that the radioactivity of potassium and rubidium compounds is strictly proportional to their respective potassium and rubidium contents (40), and that the radiation has the same intensity at the temperature of liquid air as at room temperature (41)

Since the emission of a β-particle should increase the nuclear charge number by one unit, it should lead in the case of potassium to the production of a type of atom $Z=20$, i e. to an isotope of calcium, and in the case of rubidium to a type of atom $Z=38$, or to an isotope of strontium (42).   We may hope to obtain information on the existence of these disintegration products from atomic weight determinations performed with calcium and strontium from different sources.

XXV

EFFECTS OF THE RAYS FROM RADIUM

THE effects produced by the rays from radium may be grouped in the following way :

    1. Photographic Action.
    2. Ionisation
    3 Excitation of Luminescence.
    4 Development of Heat.
    5. Chemical Effects.
    6. Colloido-Chemical Effects.
    7 Physiological Action
    8. Mechanical Effects.
    9. Atomic Disruption

1. PHOTOGRAPHIC ACTION

In the Introduction (p. 1) we mentioned that the rays emitted by radioactive substances exert a similar action on a photographic plate to that produced by ordinary light , where the rays have fallen, the plate becomes blackened after it has been treated with a developer. When radioactive research was in its infancy, and before the methods of measurement based on the ionisation of air had been developed, the photographic plate was the main instrument used in the study of the new phenomena, and even to-day it is by far the most suitable piece of apparatus for certain experiments. Thus, in the experiments on Röngten spectra it has been shown that photography enables us to work in a much simpler and more exact manner than does the ionisation chamber, which was originally utilised, and in a similar way the " spectra " of β-rays obtained by deflection in a magnetic field are best registered on a photographic plate (cf. Fig. 10, Plate I) It can also serve the purpose of enabling us to follow the tracks of α-particles in an accurate fashion ; a tiny particle of a radioactive substance that emits α-rays (*e.g.* polonium), when laid on a photographic plate, shows in all directions from the particle outwards the tracks of those α-particles which were emitted parallel

to the plate, and which " blackened " silver bromide nuclei that lay
in their path.   In mineralogy it is often useful to be able to establish
the position of a radioactive inclusion in a mineral ; a photographic
plate laid on the polished surface of the mineral will reveal even the
smallest active inclusion, if the experiment be carried out for a
suitable length of time.   Nevertheless, the sensitiveness of the
photographic method, e g. for the weak β-rays from radium, is
distinctly smaller than that of electroscopic measurements.

Since the β- and γ-rays are able to pass through solid substances,
in a manner dependent on the density of these substances (see p 34
and p. 46), it might occur to us to produce radiograms by means of
radium rays, similar to those produced by Röntgen rays.   They are,
however, much less suitable for this purpose.   In the case of the
β-rays, the reason is to be found in the fact that, in consequence of
the marked scattering effects, the edges of the objects radiographed
always appear blurred , but even if we deflect the β-rays by means
of strong magnetic fields, so that only the γ-rays strike the photo-
graphic plate, the radiograms obtained will still be worse from the
photographic point of view than those obtained by Röntgen rays,
because, owing to the greater penetrating power of the γ-rays, the
contrasts between the radiographed objects of greater and lesser
density are smaller.

The length of exposure necessarily varies within wide limits, de-
pending on the strength of the radioactive substance. Fig. 38 (Plate V)
shows writing which was obtained by using a strong preparation of
40 mg. of radium enclosed in a glass tube   This served as a pencil,
and was drawn slowly to and fro over the photographic plate, which
was wrapped in black paper.   It was almost exclusively the β-rays
from the preparation that were effective in this case.

The mechanism of the action of the rays from radium on the
silver bromide of the photographic plate is certainly akin to that of
light, and the same theories (quantum theory, colloido-chemical
ideas, etc.) must be applied here for an explanation of the effects.
In this connection, it is probable that the γ-rays do not act directly,
but that here the same peculiar fluorescence of the silver or bromine
atoms manifests itself, as makes the plates so particularly sensitive
to Röntgen rays (1).   With α-rays it has been established that every
silver halide nucleus struck by a single α-particle becomes blackened
after development, whereas on the average 6 to 8 β-particles are
necessary to make a silver halide nucleus capable of development.

At those places on the gelatine film that are most strongly bombarded by α-particles, indentations occur ; the swelling capacity of the gelatine is reduced.   Moreover, marked solarisation effects are observed on those parts of the plate that have been subjected to the action of strong sources of α-rays.   After a certain duration and intensity of the action has been exceeded, the plates are found to be blackened even before they have been developed (2).

Bunsen and Roscoe's law of blackening holds not only for the β- and γ-rays (3), but also for the α-rays (4).

An interesting illustration of the photographic action of the radioactive rays is shown in Fig. 39 (Plate VI), which is an auto-radiogram of various organs of a rabbit, taken by means of the α-rays emitted from polonium that had been injected into the organs (5).

2. IONISATION

This action of the rays from radium has already been described (p. 7), and we have seen that the ionisation of the air forms the basis of the whole of the technique of radioactive measurements.   It may be added, however, that solid and liquid dielectrics also become conducting under the influence of the rays from radium, in a similar manner to gases.   The behaviour of hexane, a liquid hydrocarbon with the formula C_6H_{14}, is of interest.   Ions of mobility 10^{-4} are produced in this liquid, and this corresponds to the value for electrolytic ions. On the basis of this result we may assume that the small conductivity always shown by hexane is to be attributed wholly or in part to the action of the natural penetrating radiation (see p. 222)   Since the number of ions produced in the unit of time is only small, the phenomenon of the saturation current manifests itself here, just as in the ionisation of gases (cf. the Note on p. 15).

It has also been shown that the conductivity of pure water increases under the action of the radiation.   But in this case it is not quite certain whether we have here an actual increase in the conductivity of the water itself, or whether the rise is due to the solution of some of the material of the walls of the vessel under the action of the rays, and the consequent addition of a trace of an electrolyte. In view of the extreme sensitiveness of water towards small amounts of impurity, the latter possibility cannot very readily be excluded

The ionising action of the rays from radium is sometimes also used in other physical measurements apart from in radiological ones. By this means, for instance, we can investigate the contact potential

PLATE VI

Fig 39 (p 192)

Auto-Radiograms of Organs of Rabbits into which Polonium had been injected

1 and 2, Kidney, 4 Foetus, 4 Heart 5, Placenta 6 Liver, 7 Brain, 8 Lung, 9 Pancreas, 10 and 14, Lymphatic Ganglia 11 Ovary and Testicle, 12 Suprarenal Capsule, 13 Bone Marrow, 15, Intestine, 16 Spleen 17 Appendix, 18 Bone, 19 Skin 20 Thymus

between metals. Moreover, it is of especial use in atmospheric electricity measurements, where we can replace flame electrodes by ionising discs, activated with, say, polonium, in order to measure the potential of the surrounding air.

3. Excitation of Luminescence

The rays from radium, themselves invisible, possess the striking ability of being able to excite substances to emit visible light. This subject has already been mentioned briefly on p. 1, in the case of so-called *autoluminescence*. Thus, when we subject a barium salt containing radium to fractional crystallisation, the mixed barium and radium salt becomes self-luminous in the dark, when the concentration of radium in the mixture has reached a certain value. The colour depends on the proportion of radium relative to barium present in the mixture, and can, in fact, serve for the approximate estimation of the radium content of the preparation. When a 100 % preparation of radium chloride is fused, and thus completely freed from water, it emits a bluish light which is so intense that it can be seen even in bright daylight (*6*). Investigations of the spectrum of this light have shown that it consists of the band spectrum of nitrogen. Correspondingly, we obtain the helium lines in an atmosphere of helium. The phenomenon of self-luminescence has also been observed with strong solutions of radium salts, and with strong preparations of polonium, ionium, mesothorium and actinium.

With weak preparations we can only obtain the phenomenon of luminescence by bringing them near to substances which show a marked ability to fluoresce. As is well known, barium platino-cyanide ($BaPtCy_4 + 4H_2O$) and crystalline zinc-blende are very suitable for this purpose. The former is used particularly for the detection of Röntgen rays, and likewise for γ-rays, whilst the latter shows the phenomenon of " scintillation," and enables us to detect the incidence of individual a-particles. Each a-particle gives rise to a single flash of light when it strikes the screen coated with zinc-blende, and by suitably choosing the strength of the a-ray preparation, we observe, particularly with a lens, a highly characteristic phenomenon—the luminous field appears to be in a state of agitated motion, as a result of the constantly changing flashing up of individual luminous points. The duration of an individual flash of light is only 10^{-4} seconds.

Special precautions are necessary for the preparation of samples of zinc-blende which fluoresce satisfactorily. The amorphous ZnS powder obtained by precipitation from an aqueous solution does not show phosphorescence, and it is necessary to transform it into the crystalline form by glowing it. Before the precipitation we must either arrange that there is an excess of the zinc salt present, or we must add a foreign heavy metal (e.g. copper), because even the crystalline blende is capable of phosphorescence only when so-called " nuclei " (see below) are available.

The far-reaching conclusions resulting from the fundamental investigations on the scattering of α-particles and on the disruption of atoms are based solely on the appearance of a few light flashes on zinc sulphide screens, in unexpected directions or distances This emphasises the great importance which attaches to the preparation of good zinc sulphide screens for scientific work

Preparations of zinc sulphide with which a certain quantity of a radioactive substance has been mixed are of practical importance, for they exhibit more or less permanent luminescence, which is independent of external sources of energy. These radioactive " luminous substances " differ from the phosphorescent substances formerly used, in that they do not require previous illumination. They are used for coating the pointers and figures of clocks, watches and compasses, for rendering signs visible (e.g in theatres), and bait on fish-hooks, etc. The most rational α-rayer to use for this purpose is radiothorium, since the ability of every zinc sulphide preparation to luminesce appreciably diminishes even after the lapse of a few months. For this reason it is not economic to use long-lived substances like radium or mesothorium, which are very expensive ; nevertheless, these radio-elements were used almost exclusively a few years ago. One gm. of zinc sulphide is mixed with a quantity of radiothorium, the intensity of the γ-radiation from which is equivalent to $\frac{1}{10,000}$ to $\frac{1}{10}$ mgm. of radium. When a good sample of zinc sulphide is utilised, more than 1 5 % of the energy of the α-rays is transformed into light, and this, fortunately, is for the most part distributed over the visible spectrum, with a maximum at 550 $\mu\mu$ (7).

The above-mentioned diminution with time of the ability of preparations of zinc sulphide to luminesce is most probably explicable on the assumption that the luminescence originates in the so-called " centres " postulated in all " phosphors." In zinc sulphide these

centres are present presumably only in relatively small numbers—about one in every 1000 ordinary molecules—and they are gradually destroyed by the action of the radioactive irradiation.

Apart from barium platino-cyanide and zinc-blende, a large number of substances fluoresce more or less strongly under the action of the rays from radium (8) ; thus the mineral willemite (an ortho-silicate of zinc) emits green light, kunzite (a silicate of lithium and aluminium) emits red light,* and the fluorescence of diamond is of a bluish colour. In the case of diamond, scintillations can also be observed when a-rays fall upon it (9). Moreover, most benzene derivatives luminesce under the action of the rays from radium, particularly those with many rings and the derivatives of salicylic acid, *e g.* salipyrin (=acid salicyl anti-pyrin) Furthermore, the crystalline lens, the vitreous fluid, and the retina of the eye fluoresce under the action of γ-rays , this is the reason why even blind persons, provided the retina and optic nerve are not damaged, are able to experience the sensation of light when a radium preparation is brought near their eyes

Most fluorescing substances become coloured under lengthy exposure to the rays (11) , simultaneously the fluorescence diminishes, and "*fatigue*" occurs. This fact is of practical and theoretical interest By heating only slightly above room temperature, or by illumination with light, the colouring can frequently be annulled, and at the same time the ability to fluoresce restored. This decoloration by means of heat or light is generally accompanied by luminescence and the emission of electrons (thermo-luminescence and photo-electric effect), as, for instance, with kunzite, the original rose-colour of which is changed to green by the rays, or with fluorspar, which is transformed from a green to a blue colour under the action of the rays. New vessels and tubes of glass luminesce much more strongly under the action of radioactive solutions or gases than those that have been in use for a long time. This is a striking illustration of the fact that glass fatigues or loses its ability to fluoresce under the action of the rays. Glass apparatus that has been long subject to the rays always has a brown or violet colour, and also shows the phenomenon of thermo-luminescence very clearly (in the well-known characteristic green glow of Röntgen

* Kunzite, and in a lesser degree also fluorspar and a few other crystals, can be excited to show luminescence very strongly, when they are first rayed with γ-rays, and later with ordinary light (10).

tubes).   Quartz that has assumed a violet colour also shows the same luminescence during its decoloration by means of heat.*

A unitary theoretical explanation of the phenomena described is possible on the basis of the electron theory.   The β-rays, *i.e.* free electrons, are the most effective in the production of the majority of colorations ; moreover, the γ-rays also always liberate secondary electrons (see p. 51).   The incident electrons, or indirectly the γ-rays, discharge the positive metal ions of the minerals and glasses, which latter are constituted like salts, or else they bring individual atoms composing the crystal into anomalous quantum states (see p. 64).   In these cases, where the electrons have the opportunity of establishing themselves in the crystal edifice, these disturbances may persist under certain circumstances for considerable periods, in contrast to the disturbances, say, in gaseous media (resonance disturbances), which always have an exceedingly short life.   The return from the metal-ionic or from the anomalous ionic state to the normal state, which is hastened by heating, may be associated with the emission of light (thermo-luminescence) and simultaneous decoloration, and the former process may also be accompanied by the liberation of electrons (photo-electric effect).   The colour assumed by salts under the action of the rays has often been found to agree with that of their colloidal liquid solutions (sols).   This suggests that in these cases, *e g* when sodium chloride (*12*) is irradiated, the colour is due to the separation of the metal , thus borax beads containing lithium become brown, with sodium violet, with potassium blue, and with rubidium greenish-blue, just like the corresponding sols   Salt that was originally colourless, and has become yellowish-brown under the action of the radiation from radium, and subsequently violet by heating at 200° C., behaves like the violet salt of natural occurrence.   Colour changes and thermo-luminescence do not always run a parallel course, as is shown by the case of glass that has been coloured violet.   This may lose its thermo-luminescence completely at 200° C , but it only loses its colour above 400° C.   It is only the brown coloration of glasses that disappears at the low temperatures sufficient for the manifestation of thermo-luminescence.

* Thermo-luminescence cannot be sharply delimited from " fluorescence " ; doubly refracting calcspar that has been coloured yellow thus fluoresces in red light even at ordinary temperatures.

4. DEVELOPMENT OF HEAT

The following details will serve to amplify the information already given on p. 2.

A simple experimental arrangement that enables us to demonstrate the continuous liberation of heat by radium preparations is represented diagrammatically in Fig. 40. A radium salt is situated
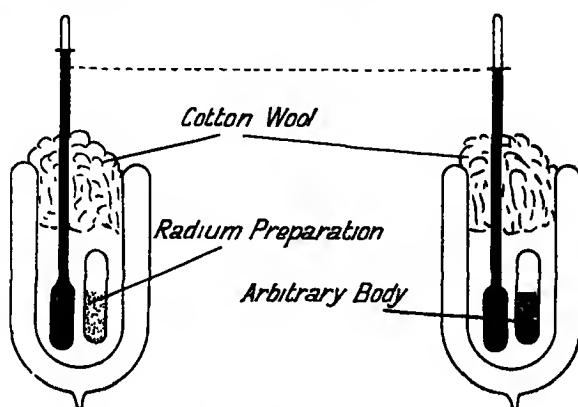
FIG. 40.   Heat Development of a Radium Preparation.

in the left of two identical Dewar vessels, each provided with a thermometer, and in the right-hand vessel the same quantity of a barium salt. The salts are sealed off in small glass tubes. The temperature in the left-hand vessel is then always somewhat higher than in the right-hand vessel. If the salt introduced contains half a gram of radium metal, the difference in temperature may amount to as much as 5° C, and is only limited by the magnitude of the unavoidable loss of heat to the exterior. Accordingly, the mercury thread in a Bunsen ice calorimeter, by means of which the amount of ice melted per unit of time is measured, moves constantly with uniform velocity.

The quantity of heat is generally determined quantitatively by evaluating the amount of electrical energy which produces the same quantity of heat as the preparation concerned (method of compensation). In setting up the experiment, of course, care must be taken to ensure that all the rays emitted are absorbed within the calorimeter, with the exception of a fraction of the γ-rays, for which a correction can be applied (*13*). In this manner it has been found

that 1 gm. of radium in equilibrium with its short-lived disintegration products develops 137 calories of heat per hour, an amount sufficient to heat 1·37 grams of water from 0° C. to 100° C.   In accordance with the slow decay of radium into the end-product lead, this generation of heat gradually diminishes.   In the time required for 1 gm. of radium to decay completely (roughly 20,000 years) it must evolve $3·7 . 10^9$ calories, for purposes of comparison it may be mentioned that about half a ton of coal would be required to produce this quantity of heat.   Even the transformation of 1 gm of oxy-hydrogen gas into water only develops 3,700 calories of heat, or only the millionth part of the above amount, and it is well known that this reaction is associated with a heat of combustion which is un-usually high for chemical changes

The following consideration leads to information as to the origin of the large quantities of heat generated by radioactive substances. From the velocity and mass of the a-rays and recoil rays, and from the energy of the β- and γ-rays (cf. p. 73), which is also known, we can calculate the total energy liberated by the preparation in the form of rays   For complete absorption of the rays, this energy must be transformed into heat.   In this way we obtain for the amount of heat resulting solely from the absorption of the rays from 1 gm. of radium, together with its disintegration products, the value 137 calories per hour; of this amount about 88 % are produced by the a-rays, 2 % by the recoil rays, 4 % by the β-rays, and 6 % by the γ-rays (14).   Since the quantity of heat found experimentally agrees well with this value, we can conclude that the heat developed by radioactive substances is due exclusively to the energy of the rays, and not, say, to other inter-atomic processes in addition.

By means of sensitive apparatus it can also be proved that polonium, and even thorium and uranium, are continuous sources of heat, exactly as we should expect from the disintegration theory. One gm. of uranium, in equilibrium with its disintegration products, generates about $9 . 10^{-5}$ calories per hour

5. CHEMICAL EFFECTS

(Note.—The study of the chemical effects of the rays from radium is sometimes called " radio-chemistry " in the narrower sense, analogous to the designation " photo-chemistry " for the study of the chemical effects produced by light.   Here, and in the rest of the book, however, we shall understand by radio-chemistry the chemistry

of the radio-elements, *i.e.* the study of their chemical properties and reactions, since there is no other short name available for this much greater and much more important branch of the science.)

It has already been mentioned that many similarities exist between the chemical effects produced by the rays from radium and those produced by light. In our discussion of the ionisation in gases we associated it with the better known case of electrolytic conduction. It will serve a useful purpose if, in the individual examples and in the theory of the phenomena of the chemical effects of the radium rays, we likewise always draw attention to the analogous photo-chemical effects. We shall first discuss a few examples of chemical changes resulting from the action of the rays from radium.

(a) Chemical Effects in Solids

Colourless glass becomes coloured under the action of the rays from radium ; ordinary sodium glass and glass containing manganese becomes violet, whilst glass containing iron or potassium becomes brown (see also p 195). The coloration is annulled by the action of light, and more quickly still by the action of heat, and at the same time the phenomena of luminescence already mentioned make their appearance. Precious stones and minerals also alter in colour ; thus, diamond is superficially transformed into graphite, blue sapphire becomes yellow (synthetic sapphires remain unchanged), bright green fluorspar becomes dark blue, red kunzite green, and colourless rock-salt blue or brown. The pleochroic haloes that are visible in many minerals (see p. 216), and which are a consequence of radioactive inclusions, show the same colorations as we can produce by artificially raying the same minerals. It is well known that many glasses also assume a yellow, green, or violet colour when they are subject to the action of light for a long period or when the intensity of the radiation is large.

• One of the best-known photo-chemical effects is the bleaching of dyes. An analogous destruction of the colour by means of radium rays has also been detected, *e.g.* with indigo or chlorophyll. These reactions are more obvious in solutions or with strips of material soaked with solution than when the dye is in the compact solid form.

The destructive action of light on paper containing lignin, in the presence of air, is well known. The rays from radium exert a much more energetic destructive action on every kind of paper, on silk,

linen and celluloid.   The action is probably due to oxidation by the ozone that is produced by the rays.   In a similar manner, paraffin wax, vaseline and rubber become hard, and tap-grease is decomposed with evolution of CO_2 by the action of the rays.   These phenomena must be taken into consideration in the construction of apparatus for radioactive purposes.

Yellow phosphorus is transformed into the red variety under the action of light , exactly the same effect has been observed with the rays from radium.   When light is incident on selenium, its electrical resistance is found to diminish, and this fact is utilised in numerous processes such as light-telephony, and the ignition of explosives at a distance.   The resistance of selenium also decreases when radium rays are incident upon it   Nitrogen iodide explodes instantaneously when subject to the light from burning magnesium ; about 20 secs. are required before the explosion takes place when the nitrogen iodide is submitted to the a-radiation from 3 millicuries of emanation at a distance of 1 cm (15).   It follows from this that only one in 10^7 or 10^8 a-particles is effective in bringing about an explosion.

The reducing action of radium rays on silver chloride and silver bromide is also of great importance, and quite analogous to the action of light.   It constitutes the basis of the photographic action of the rays, and for this reason it has already been mentioned (p. 190).

(b) Chemical Effects in Liquids

The decomposition of water under the influence of the rays from radium is of particular importance   In this process, gases consisting of H_2, O_2 and O_3 are liberated, and simultaneously a little hydrogen peroxide is formed in the water.   We can picture the processes by means of the following two equations :

$$2H_2O = 2H_2 + O_2,$$
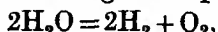
(a part of the O-atoms initially formed goes to form ozone with the O_2), and $$2H_2O = H_2O_2 + H_2.$$

Most of the water molecules decomposed follow the first reaction, and so form oxy-hydrogen gas, but owing to the second reaction there is always an excess of hydrogen mixed with it.   The amount of the decomposition products obtained from a given quantity of a dissolved radium salt depends on two factors.   First, it depends on the fraction of the a-, β- and γ-rays absorbed in the water, and thus on the dimensions of the vessel, and secondly, it depends particularly on the magnitude of the gas space over the liquid,

because the relative distribution of the emanation between the liquid and the gas is determined by this (cf. p. 178). As an approximate estimate, it may be stated that a daily production of 13 cc. of gas has been observed from 1 gm. of radium in solution.

This continuous evolution of appreciable quantities of oxy-hydrogen gas can give rise to much trouble when radium preparations are sealed off in glass tubes before being completely dry. The pressure of the gases developed may burst the tube, and a slight and sudden application of heat may result in a veritable explosion. For this reason, it is absolutely necessary, before sealing off strong preparations, to maintain them at a temperature of over 100° C. for a few hours.

If only the penetrating rays from radium are used for the decomposition of water, the velocity of decomposition is very much smaller, e.g. when the radium preparation is enclosed in a double-walled vessel filled with water. It can be increased by enclosing the outer vessel in a sheath of lead. In this case, secondary β-rays are emitted by the lead, and since they are absorbed by the water more strongly than the primary γ-rays, they give rise to a bigger effect. This experiment has been mentioned because it presents a certain formal analogy to so-called " optical sensitisation " ; thus, a photographic plate becomes sensitive to red rays when it contains eosin, and, after the addition of chlorine to a mixture of hydrogen and oxygen, the last two gases are made to combine by those rays that are absorbed by the chlorine, whereas in the absence of chlorine the action of visible light is only a slow one.

The decomposition of water by the two reactions mentioned above can also be brought about by means of light, particularly by ultra-violet light

It has been mentioned that a certain amount of hydrogen peroxide is formed from water under the action of the rays from radium (16). The reverse reaction is more markedly influenced by the rays, i.e. the decomposition of hydrogen peroxide. Ultraviolet light produces the same effect ; in fact, a mercury lamp acts incomparably more quickly than even a strong preparation of radium.

From amongst other reactions which take place in liquids, we may mention that in the mercury oxalate actinometer oxalic acid is decomposed by the rays as well as by light :

$$2HgCl_2 + C_2O_4(NH_4)_2 = Hg_2Cl_2 + 2CO_2 + 2NH_4Cl.$$
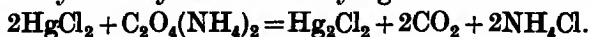
The amount of calomel precipitated, or the amount of carbon

dioxide liberated serves as a measure of the intensity of the light. Additional reactions that have been described are in complete qualitative agreement with the transformations wrought by light, but in general they take place several hundred times more slowly than when a mercury lamp is used as the source of light. The following are examples of such reactions : the liberation of iodine from a solution of iodine in chloroform ; the decomposition of liquid HBr or an aqueous solution of HBr, or of HI or KI solutions ; the separation of silver from dissolved silver nitrate ; the decomposition of nitric acid into nitrous acid, nitric oxide and oxygen.

It has been observed that platinum vessels are attacked by solutions of radium chloride. This is explained by the liberation of nascent chlorine, which in its turn dissolves the platinum.

(c) Chemical Effects in Gases

The most striking of these is the formation of ozone from oxygen ; the characteristic smell of ozone is detectable in the proximity of every preparation that is emitting intense radiation. In consequence of this, metals like mercury, lead, aluminium, and also paper, linen, etc. (see above, p. 199), are oxidised after a longer or shorter period of time, when they are situated near to radioactive preparations. In glass flasks filled with pure nitrogen, the walls of which contained different substances (Na, K, S, P, I, As, Mg, Hg), a decrease in pressure has been observed under the influence of a-rays. This is obviously caused by gas absorption by the walls of the vessel or by the experimental substance (17). The formation of ozone, in particular, has also been accurately investigated quantitatively, but we shall defer details of this work until we are discussing the theory of the chemical action of the rays (see p. 205).

We meet with additional syntheses from gaseous constituents (18) in the formation of ammonia, water and hydrobromic acid from the respective elements, but these reactions are restricted by the reverse reactions, namely, the decomposition into the elements   Decomposition is more frequently observed : thus CO_2 is resolved into C, CO and O ; CO is resolved into C and O. Here also we have to consider the equilibrium conditions, and radioactive radiation also favours the reverse process. The same thing holds for the reaction between hydrogen and chlorine : $H + Cl \rightleftharpoons HCl$.

The photo-chemical processes corresponding to these transformations are so well known that we need hardly enter into a discussion of them here.

(d) General Nature of the Chemical Reactions produced by the Rays from Radium

We have not classified the reactions referred to above to indicate whether they are caused by a-, β-, or γ-rays, because in many cases details on this point are not available, and in most of the cases in which the part played by the different kinds of rays has been studied, it has been found that all three produce the same alterations. In general, we can say that the a-rays have the strongest action, if this is not prevented by their ready absorbability. Most reactions with gases have been carried out with radium emanation, in which case the major part of the action can certainly be ascribed to the a-rays ; likewise for the decomposition of water into oxy-hydrogen gas, which has also been established by the use of polonium, which emits only a-rays, and similarly for the breaking up of nitrogen iodide. Small quantities of radioactive substances can only bring about colorations in glass to a depth of a few hundredths of a milli-metre, and this corresponds exactly to the phenomenon of pleochroic haloes (see p. 216), in which the simultaneously emitted β- and γ-rays also have no appreciable action.

In other reactions the β-rays are mainly responsible for the changes, for they are able to penetrate more deeply. Particularly in the separation of iodine from iodoform in benzene, a-rays are pre-sumably quite ineffective. Like ultraviolet light, β-rays decompose water into hydrogen peroxide and hydrogen, in contrast to a-rays.

The absorption of γ-rays is so small that their action cannot be large, owing to the small losses of energy involved (re sensitisation for γ-rays, cf. p. 201).

From the illustrations that have been mentioned, it is clear that, both in solids and in liquids and gases, the chemical actions produced by the rays from radium are extraordinarily similar to those of light, at least in their outward manifestations. Many reactions are quite identical ; and this is particularly true of those caused by the penetrating rays, in which case the radioactive preparation used in the experiment is enclosed in a glass tube. From the theoretical viewpoint this agreement can be readily understood, for the γ-rays are nothing else than light of very short wavelength. When the more readily absorbable rays are also admitted, the effects are very much stronger, but even then they are in all probability not different qualitatively from those produced by light. Nevertheless, under

such conditions reactions like the marked formation of ozone take place quickly and in appreciable degree, even when they would be hardly perceptible by the use of light.

A further similarity with photo-chemistry is particularly embodied in the fact that one and the same reaction is often favoured in both' directions.   But whereas in the case of light, *e g.* with hydrobromic acid, it has been established that different wavelengths produce effects opposed to each other, such a distinction has not hitherto been observed by the use of the rays from radium.   Thus emanation decomposes water, and at the same time brings about the combination of oxy-hydrogen gas.   An analogous behaviour is found with ammonia.   Attention is sometimes drawn to the surprising fact that in certain cases light produces effects the reverse of those due to radium rays, as when colorations in minerals due to the latter rays are made to disappear by the action of illumination by light.   But we need see nothing surprising in this, when we remember that the effects produced by different kinds of light are often opposed to each other.

Of especial importance is the fact that the temperature coefficient of the reactions effected by the rays from radium is just as small as in photo-chemical reactions , it has been found to be 1·2 per 10° C. for the decomposition of hydrogen peroxide.

(e) *Theory of the Chemical Reactions produced by the Rays from Radium*

Since the outer manifestations of these reactions and those of photo-chemistry have been found to resemble each other so closely, we may ask ourselves whether we may assume that the mechanism of the changes is also the same in the two cases   The answer is in the affirmative.

Great strides have been made in the theoretical treatment of photo-chemical processes during recent years.   By using thermo-dynamic principles as a basis, the tendency of a few years ago was to introduce a strict differentiation between those processes which take place as a result of the absorption of energy from the light, and those in which the light accelerates the action in a catalytic fashion. But it has now been recognised that reactions which run a quite similar course must often for some reason or other be treated separately.   The mechanism of the processes was first revealed by considering them from the atomistic viewpoint, by means of Einstein's

" photo-chemical law of equivalence." If we divide the absorbed
energy of radiation by the value of Planck's element of energy
corresponding to the wavelength used, then by the equivalence law
we must obtain the number of the elementary processes involved in
the experiment. In point of fact, it was found, *e.g.* when oxygen is
subject to ultraviolet radiation, that the number of elementary
processes calculated in this manner is of the same order of magni-
tude as the number of molecules of ozone formed. To be more
exact, twice as many ozone molecules are formed, and hence we may
assume that in every elementary process one O_2 molecule is split
up, and the resulting $2O$ combine with two additional O_2 molecules
to form $2O_3$.

The idea suggests itself of interpreting the elementary process as
the separation of an electron from the atom, or as the elevation of
an electron to a higher quantum orbit, and in this way to establish
a relation between the amount transformed and the number of the
electrons taking part in the reaction   This relation was clearly
revealed in an electro-chemical investigation akin to the photo-
chemical one described   In this work we recognise, in a particularly
striking manner, the close connection with the reactions produced
by the rays from radium. The formation of ozone from oxygen
under the influence of Lenard rays was here also investigated (*19*).
Cathode rays were passed through an aluminium window into a
vessel containing oxygen, and the amount of ozone formed was
determined , moreover, by measuring the saturation current, it was
also possible to determine the total number of ions produced in the
reaction vessel.   Whereas the number of primary electrons shot into
the vessel was one hundred to one thousand times smaller than the
number of ozone molecules formed, a good agreement was found to
exist between the number of the ozone molecules and the number of
secondary pairs of ions produced in the reaction vessel.   A single
electron can give rise to many thousands of ions when it ionises by
collision (cf. p. 37), and it is obviously these secondary ions which
call forth an equally large number of elementary chemical processes
in accordance with the photo-chemical law of equivalence.   The
fact that the number of ozone molecules was always found to be
somewhat larger than the number of pairs of ions speaks in favour of
the idea mentioned above, according to which even those electrons
that are not separated from the atom but only raised to a higher
quantum level, and which therefore do not contribute to the satura-

tion current, are nevertheless to be taken into account for the law
of equivalence.

Now an exactly similar calculation of the number of electrons
taking part in the reaction is also possible for the rays from radium.
Here also it is a question of an electrical conductivity caused and
sustained by an outside ionising agency, and the number of ions
contributing to the conduction of electricity is much greater than the
number of primary particles entering the gas, the former number
sometimes being as much as 10^5 times the latter (cf. p. 26). Now
the total number of pairs of ions produced by a radium preparation
of definite strength can readily be found from the saturation current.
In the formation of ozone from oxygen under the action of the rays
from radium emanation, it was thus possible to compare the number
of ozone molecules formed with the number of pairs of ions produced,
and when this was done it was found that the requirement of equi-
valence was excellently confirmed within the limits of experimental
error (20). As in the case previously mentioned, we should here
obtain much too small a value for the number of elementary chemical
processes if we were to regard the charges carried by the a-particles
shot into the gas as being the determining factor in the reaction,
instead of those of the pairs of ions formed.

This equivalence between the number of molecules entering into
chemical reaction and the total number of ions formed by the a-rays
has been proved not only in the formation of ozone, but also in the
formation of water, ammonia and hydrobromic acid from the
constituent elements, and also in the decomposition of hydrochloric
acid, ammonia, CO and CO_2. Moreover, it has also been established
in liquid systems, e g. in the decomposition of water, liquid hydro-
bromic acid, and in an acid aqueous solution of potassium iodide.
In accordance with this equivalence, it has been possible to show that
a definite chemical transformation is associated with the presence of
a definite number of ions, in a similar manner as in Faraday's law.
In contrast to Faraday's law, however, these ions must not participate
in the transport of current, and hence in this case we generally only
speak of an " *iono-chemical equivalence* " (21).

Chemical actions are here brought about in a roundabout way
by the formation of excited atoms or of ions. The recognition of
this fact renders it intelligible why the utilisation of the radioactive
energy in its transformation into chemical energy is such a poor one,
both with light and with the rays from radium. On the assumption

that the first step in the process is complete ionisation, $5 \cdot 5 \cdot 10^{-11}$ ergs must be consumed in the formation of a pair of ions in air. According to the ideas developed above, one such pair of ions can entail the chemical transformation of only one molecule. Now the greatest heat of reaction in such a transformation, and we shall regard this as a measure of the free energy, amounts to $6 \cdot 9 \cdot 10^{-12}$ ergs, so that only about 12 % of the aforementioned energy can be stored up in the form of chemical energy, and since in general more than one pair of ions per molecule is necessary, and the heat of reaction is smaller than the above amount, it follows that the utilisation of the energy is as a rule still worse (2-3 %). The calculation works out more favourably when we do not assume complete ionisation but only the excitation of a molecule as the preliminary step in the reaction. In a photo-chemical reaction, for which the efficiency is just as small as in the above case, we are probably justified in assuming that here also the process takes place through the intermediary of an anomalous quantum state (p. 64) or a transitory ionisation of the atoms.

It is particularly noteworthy that the iono-chemical law of equivalence also holds when the chemical reaction takes place in the direction of the free energy, so that here also a much greater radiative than chemical energy is involved   It makes absolutely no difference in the number of ions requisite that no chemical energy whatsoever must now be stored up , the large thermodynamic difference can be ignored entirely, and from this we may conclude that even in such cases we must not regard the action of the rays as being of a catalytic nature (cf what was said above on the untenability of the older division into two categories) The experiments supply unequivocal evidence that the effectiveness, say, of emanation is of the same order for a reaction which proceeds in the direction of its own free chemical energy, as for one that proceeds in the reverse direction. Moreover, quite similar observations have been made in the field of photo-chemistry , thus, in the decomposition of ammonia by means of ultraviolet light, it has been established that the same intensity of the light is necessary for the decomposition of a particular quantity of ammonia, no matter on which side of the thermodynamic equilibrium we may be. Thus, in all cases hitherto investigated, both light and the rays from radium appear to allow chemical reactions to proceed along their natural course, which is marked by the expenditure of large quantities of energy. Moreover, every advance in our knowledge of the mechanism of photo-chemical

reaction will also supply us with new information on the course of chemical transformations brought about by the action of the rays, from radium.

6 COLLOIDO-CHEMICAL EFFECTS

In this section we shall discuss individual effects produced by the rays from radium, in so far as they stand in particularly close relation to questions in colloidal chemistry. It is of course not possible to delineate a sharp boundary with respect to the topics hitherto dealt with. Thus it is known that the photographic process, of which we have previously spoken, must also be considered from the colloido-chemical viewpoint, and the colorations dealt with on p. 196 likewise present certain colloido-chemical problems for solution.

The study of the action of the rays from radium on the stability of colloidal solutions belongs to colloido-chemical investigations in the narrower sense. In this connection, the following interesting result has been established, namely, that positive colloids are precipitated, whereas negative ones survive the radiation. The experimental arrangement was so chosen that almost exclusively β-rays were involved in the action, and since these carry negative charges, we can understand why they deposit the positive colloids. Thus, if we add to a colloidal solution of iron hydroxide a quantity of, say, sodium acetate solution, just insufficient to produce a change, we can then obtain turbidity of the colloid by means of radium rays, whereas a control sample that has not been subject to radiation will remain unchanged. With a sol of cerium hydroxide it is not even necessary to sensitise it previously by means of an electrolyte; by subjecting the sol to radiation it is transformed into a coherent gel even after a period of 24 hours whereas it remains unchanged for years when not submitted to the action of radiation (*22*)

None of the electro-negative colloids gold, molybdenum blue (an oxide of molybdenum containing water), and vanadium pentoxide, the last of which tends to form a gel just like cerium hydroxide, were influenced when subject to radiation. Albumin, which also forms electro-negative colloidal solutions, is deposited in flocculent masses, but it is probable that this is not simply a phenomenon of discharge, but rather that the albumin first loses its original nature (*22*).

Under certain conditions, the rays from radium are also able to bring about the formation of cloudy deposits. Thus if we introduce into a closed vessel distilled water, a piece of sulphur, and radium

emanation, the air space is continuously filled with a cloudy suspension. Since we can detect traces of sulphuric acid in the water, the explanation of the phenomenon undoubtedly seems to be that SO_2 and thence SO_3 molecules are produced by the action of the radium rays, and that these serve as condensation nuclei for water vapour; visible fumes must be formed in exactly the same way as when, say, hydrochloric acid gas escapes into the moist air of a room. When sulphur has not been introduced into the vessel, we only obtain a very much weaker cloudiness. It is probable that in this case the nitrogen oxides formed by the action of the rays from the emanation give rise to just sufficient condensation nuclei to form a cloud, for if we replace the air by carbon dioxide, we can no longer observe a permanent cloudy effect.

If we use *super-saturated* water vapour, condensation occurs directly on the ions formed, and chemical reaction is unnecessary. This method is utilised to render visible the tracks of the rays from radium (see p. 78).

The following observation is also undoubtedly more or less closely related to the facts already described. By means of β-rays it is possible to increase the rate of crystallisation of supercooled sulphur. If only a fraction of the drops of sulphur has been rayed, many more crystallisation nuclei are found amongst these drops than amongst those that have not been so treated.

7. PHYSIOLOGICAL EFFECTS

Not long after the discovery of radium it was observed that this substance must not be handled without precaution. If we allow a strong radium preparation to lie for some time on the skin, sores develop, which are very similar in appearance to a burn. Whereas in the case of the action of heat, however, our attention is drawn to the danger by the resulting pain, the rays from radium have the sinister property that they do not at first give rise to any unusual feeling; with a strong preparation it is not until several days or a week or two later that the inflammatory process begins. Particularly in the earlier days of radioactive research, when the danger had not yet been recognised, many radiologists suffered from such sores on their fingers. In many cases a marked atrophy of the affected finger tips developed, and there is a danger of cancer developing later, just as in the case of burns by Röntgen rays.

After it had been established that the rays from radium have a physiological action, it was suggested that they might have an application in medicine, and as a matter of fact it is possible to produce satisfactory improvement in various skin diseases, whereas healthy skin is damaged by the rays.   The penetrating rays often have a healing or at least a favourable and soothing action on internal diseases, particularly in cases of carcinoma.   In most cases normal tissue is from four to seven times more resistant to the effect of the rays than diseased tissue.   Moreover, much success has been attained in cases of gout and rheumatism, and recently science has been inclined to attribute the healing action of many natural springs to their content of radium emanation.   A decrease in the leucocyte content of the blood has been observed as a result of the injection of radioactive solutions, and it may be possible to make use of this fact in cases of leucocythaemia.

The underlying processes are not only of great importance in medical practice—on which subject further information can be obtained from the extensive literature of medical radiology—but they are also of undoubted interest from the viewpoint of theoretical biology, in which connection they have been frequently investigated   We can only discuss here the most important of the experimental results

Irritants which are harmful to an organism when administered in large doses often have a favourable influence when used in small doses.   In this connection we may recall the fatal action of large quantities of many compounds used in medicine.   Now this general rule, which has even been called a " fundamental law of biology " (23), has been completely confirmed in its application to the influence of the rays from radium.   Young plants exposed to the rays from radium are found to exhibit a distinct improvement in their growth when only small doses are used, whereas large doses are highly detrimental to the development of the plants, as can be seen from Fig. 41 (on Plate VII) (24).   By the action of a sufficiently strong source of radiation we can destroy the vitality of seeds, and kill bacteria (cholera, typhus, anthrax. streptococcus) and also higher animals such as caterpillars.   Germ-cells are particularly sensitive , if we subject ova or spermatozoa to the action of the rays we can observe different kinds of developmental arrest.   Changes in the cells which cannot be detected even with the highest magnification make themselves manifest in the further development by the appearance of deviations from the normal development.

PLATE VII.

FIG 41 (p 210)
Action of Radium Emanation on Shoots of *Phaseolus multiflorus*

From left to right the samples indicate the effect of a large and of a small quantity of emanation, whereas the right-hand illustration is that of a control specimen, without emanation

FIG. 42 (p 217)   Pleochroic Haloes

A former contention of a specific action of the rays on physio-logico-chemical compounds *in vitro* has not been verified. On the other hand, β-rays have a marked capacity for haemolytic action, and this fact may perhaps be made use of in connection with their application in medical practice (*25*).

The danger of burning the fingers, which is considerable where strong radium preparations are often handled (*26*), can be best obviated by the use of rubber finger caps pulled over the ends of the fingers which actually come in contact with the tubes containing the substance. They suffice to screen off the soft β-rays, which appear to be mainly responsible for the burns, and they are to be preferred to harder material, because in the latter case secondary β-rays may be produced by the γ-rays incident upon it. But the chief advantage resulting from their use is the absence of any hindrance to the handling of the preparations when one is working with them (*e.g.* in transferring material from one tube to another, etc).

Radium burns are especially troublesome, because it frequently happens that even if they mend there remains a supersensitiveness of the skin, and the rays from quite a small quantity of radium are sufficient to give rise to a renewed inflammation. We are here dealing with what is, from the theoretical point of view, a very interesting case of " indirect " or " physical anaphylaxis " (*27*) ; the anaphy-lactogens are not directly introduced into the organism as in ordinary anaphylaxis (*e g.* as a foreign type of albumen), but are formed in the organism by the action of the rays.

It should be mentioned in conclusion that very many biological reactions have been foolishly expected of the rays from radium, and even affirmed. They have actually been regarded as bringing about spontaneous generation.

8. Mechanical Effects

The mechanical effects are always brought about by electrical or by chemical actions, *i.e.* only by indirect means.

Thus, when it was observed that glass tubes into which radium had been sealed exploded, the cause of this was to be found in the excessive pressure brought about by the development of oxy-hydrogen gas (see p. 200). The assumption of electrical discharges, which have sometimes been held responsible for this effect, appears to be quite superfluous.

The so called " *radium clock* " provides a pretty experiment for

demonstration purposes, and illustrates how the rays from radium may be utilised indirectly to give rise to motion   It consists of a small glass tube containing radium, supported on an insulating support inside a somewhat wider evacuated glass tube, and having on its lower extremity two electroscope leaves.   Since the β-rays penetrate the inner glass tube and thus continuously conduct away negative charges, whereas the positively charged a-rays are retained by the tube, it follows that the latter will become more and more positively charged.   In consequence of this the electroscope leaves become more and more deflected until they touch the glass walls of the outer vessel, when they are discharged and collapse, and the whole process is then repeated time and again with the regularity of a " clock."   The charges collected on the inner glass tube in such an arrangement may suffice to raise it to a potential of several hundreds of thousands of volts.

The phenomenon of the so-called '' ionic wind '' is of great theoretical interest (28).   The a-rays show this effect best, but β- and γ-rays are also effective.   When the air between the plates of an ionisation chamber is ionised, then on applying an electric field, the air between the plates is set in motion.   The direction of this current of air is from regions of stronger to regions of weaker ionisation.   It is caused by the fact that the ions exert a dragging action on the surrounding molecules of air.   Even when the distribution of ionisation in the chamber is uniform, an ionic wind can still be detected, since the dragging action of the positive ions is somewhat greater than that of the negative ones.

9. Atomic Disruption

The phenomenon of atomic disruption is the most potent action caused by the rays from radium, and has been produced by no other agency.   Owing to its importance from the viewpoint of our conceptions on the structure of atoms, it has already been discussed in another part of the book (p. 147).   Theoretically, it is the most important application of the source of energy rendered available by the rays from radium, and it will suffice here if we once again direct attention to it.

RADIOACTIVITY IN GEOLOGY AND IN GEO-PHYSICS

1. DETERMINATION OF THE AGE OF MINERALS

THE velocities of radioactive decay are independent of all external conditions, and constitute natural constants characteristic of the disintegration process concerned. For this reason they can be utilised for the measurement of time. Since they supply us with the functional relation between the amount of the substance transformed and the time, it is clear that the velocity of decay enables us to calculate the latter quantity when the former is known. Thus, we can readily recognise the lapse of an hour without the aid of a clock, if we notice that the activity (measured, say, by a method of steady deflection) of a preparation of ThC falls to 49 % of its initial value during this time. Such methods for the measurement of time have actually attained great importance in geology, the most important of them being the following :

(a) Determination of the uranium-lead content of uranium minerals ;

(b) Determination of the helium content of radioactive minerals ;

(c) Estimation of the intensity of coloration of pleochroic haloes.

In all three cases we can readily calculate the time necessary for the attainment of the values found.

(a) Age Determination from the Uranium-lead Content

We have already seen that uranium, during its successive disintegrations, suffers the loss of eight α-particles before it reaches the stable end-product RaG, which is a type of lead. The following equation represents this transition :

$$U \longrightarrow 8He + RaG.$$
$$238 \qquad 32 \qquad 206$$
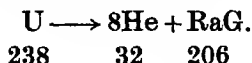
* Strictly speaking, $U \longrightarrow 8He + 0\ 97RaG + 0\ 03AcD$, since only 97 % of the uranium atoms traverse the series via radium and become RaG, whereas 3 % supply the end-product AcD after traversing the actinium series. But the neglect of this slight deviation is without influence here, the more so since AcD probably has the same atomic weight as RaG.

From this, and from the disintegration constant of uranium
($\lambda = 1\cdot4 \cdot 10^{-10}$ year^{-1}) it follows that 1 gm. of uranium produces in
one year an amount of RaG equal to $1\cdot4 \cdot 10^{-10} \cdot \dfrac{206}{238\cdot2} = 1\cdot21 \cdot 10^{-10}$
gm.   Thus if a mineral contains $1\ 21 \cdot 10^{-2}$ gm. of RaG to every 1 gm.
of uranium, it follows that the age of the mineral is 100 millions of
years.   In general, the age of a mineral in years is found by this
method by dividing the amount of RaG corresponding to 1 gm. of
uranium by $1\cdot21 \cdot 10^{-10}$, or by multiplying it by $8\cdot2 \cdot 10^9 = 8200$
millions.   In this calculation, it has not been taken into account
that in the course of this long time the quantity of uranium will have
appreciably diminished as a result of disintegration, and that a
somewhat lesser time must have been sufficient to produce the
amount of RaG found, from the previously greater quantity of
uranium.   To a first approximation we do justice to this correc-
tion by utilising the following formula for the determination of
the age of the mineral :

$$\text{Age} = \frac{\text{RaG}}{\text{U} + 0\cdot58\ \text{RaG}} \times 8200 \text{ million years,}$$

where RaG is the uranium-lead content and U the uranium content
of the mineral concerned *   Thus for the uranium pitchblende from
Morogoro (Tanganyika Territory) the ratio RaG/U $= 0\cdot093$ was
obtained, whence it follows that the age of this mineral is 700 millions
of years.   In a similar way, the age of Norwegian Bröggerite, for which
the ratio $\dfrac{\text{RaG}}{\text{U}} = 0\cdot127$, works out to be 950 millions of years (1).

Whereas the Morogoro ore contains no ordinary lead, most
uranium ores have become more or less contaminated by ordinary
lead in the process of geological changes   In utilising the analysis
of the mineral, we must be able to differentiate between this disturb-
ing lead content and that of RaG, and this necessitates the perfor-
mance of an atomic weight determination of the mixture of lead
isotopes (RaG + Pb) under consideration, from which the Pb and
RaG contents of the mineral can immediately be calculated.   Thus
the mixture of lead isotopes extracted from uraninite from North
Carolina is found to have an atomic weight of $206\cdot4$, from which it

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* The exact formula for the required age (t) is :

$$\frac{\text{RaG}}{\text{U}} = 0\ 87\ (\lambda t + \tfrac{1}{2}\lambda^2 t^2 + \ldots).$$

follows that 70 % of the atoms of this mixed element are composed of RaG.*

The stable end-product of thorium is also an isotope of lead, and if the mineral contains thorium, the thorium content must also be taken into consideration in the determination of the age. Nevertheless, the number of uranium minerals practically free from thorium is quite considerable. The mineral cotunnite, a chloride of lead found at Vesuvius, contains 12 % of RaG (2).

From amongst the minerals the ages of which have been determined by the method described, a uraninite of Carboniferous age has been found to be one of the youngest (320 millions of years). This number gives us the age of the Carboniferous System, if we make what appears to be quite a plausible assumption, namely, that the uraninite concerned is a primary mineral, and has not gained access into the formation in the course of a subsequent epoch, in which case it would be secondary. The oldest mineral hitherto investigated was a zircon from Mozambique, the age of which was found to be 1500 millions of years.

On the assumption (cf. p 188) that the lead isotope ThD—the end-product of the thorium series—is completely stable, we should of course be able to determine the age of thorium minerals from their lead content in a manner exactly analogous to that used for uranium minerals. Here we must apply the corresponding simple correction for the amount of admixed uranium-lead (RaG). In this connection it has been found that the age of many thorium minerals calculated in this manner is so small (in some cases scarcely 10 million years), that we must assume that they are of secondary origin. In such a case it is not permissible to attribute the age found for the thorium mineral to the geological formation in which it occurs. It has been established empirically that it can only be assumed that the mineral is of primary origin when the ratio thorium : uranium is not greater than 3 ; only in such cases is the above-mentioned method of finding the age of the geological formation applicable.

It has not yet been definitely established whether ordinary lead is a mixed element, or of what isotopes it is composed (3).

An upper limit for the age of the earth's crust has been calculated from estimates of the mean U_1 ($7 . 10^{-6}$ gm.) and Pb ($22 . 10^{-6}$ gm.)

* $206 \cdot 4 = 0 \cdot 7 \times 206 \cdot 05 + 0 \cdot 3 \times 207 \cdot 18$, where $206 \cdot 05$ is the atomic weight of RaG, and $207 \cdot 18$ that of ordinary lead.

contents of each gram of the crustal material, and assuming that all the lead has been derived from uranium. The value found is $11 . 10^9$ years. If we make a reasonable allowance for that part of the lead which has been derived from thorium, the above estimate of the age of the earth's crust has to be reduced to $8 . 10^9$ years (4).

(b) Age Determination from the Helium Content

As mentioned above, the uranium atom undergoes eight a-transformations before it is transformed into RaG. By far the greater part of these a-particles is brought to rest within the mineral, and remains enclosed in it as gaseous helium. When a sample of the mineral is reduced to powder a small fraction of the helium escapes, and the rest can be liberated by fusion or by ignition, when it may be collected and measured. In each second of time, 1 gm. of uranium together with its disintegration products ejects $9 \cdot 7 . 10^4$ a-particles, which corresponds to a yearly production of $11 \ 0 . 10^{-8}$ cc. of helium. The required age of a mineral is accordingly

$$= \frac{\text{He (in cc)}}{\text{U (in gm.)}} \times 9 \text{ millions of years}$$

By this method we obtain values lying between $8 . 10^6$ years (for the Oligocene) and $700 . 10^6$ years (for the Archaean). Nevertheless, these numbers can only be regarded as giving the lower limit for the age of the mineral examined, in view of the fact that small quantities of helium undoubtedly escape from the mineral when it is exposed in bulk, and particularly when it is crushed

(c) Age Determination from the Intensity of Coloration of Pleochroic Haloes

The a-rays produce coloration in glass, quartz, mica and similar materials (see p. 199), the depth of coloration depending on the number of the a-particles that traverse the material. A strong radium preparation calls forth an appreciable coloration in the course of only a few hours, but the same effect could be produced if a preparation of one millionth the strength were allowed to act for a million times as long a time. It follows that we can construct an empirical scale of colorations, produced, say, in mica by different amounts of radium during the course of a day. By means of this scale we can evaluate the time that would be necessary for an active substance of known strength to act on the mica in order to produce a given depth of coloration.

Such colorations actually occur in natural minerals. Thus we are familiar with varieties of the following minerals that have been coloured by means of α-rays : rock salt, fluorspar, spinel, garnet, tourmaline, cordierite, karpholite, mica, hornblende, chlorite, ænigmatite and staurolite (5). α-particles are emitted radially from the small radioactive inclusions in such minerals, and produce coloration within a sphere of radius equal to the range of the particles. In thin section these appear to be circular, and when examined in polarised light they show the property of " pleochroism "—whence the name " pleochroic haloes." Fig. 42 (Plate VII, p. 210) gives a highly magnified reproduction of the various dark coloured rings produced by the successive α-radiations from a tiny inclusion in fluorspar of a mineral containing uranium. In consequence of their small range, the α-rays from uranium only produce coloration in a small circular patch of radius 0·013 mm. surrounding the point inclusion in mica (6), but the coloration resulting from the action of the more penetrating α-radiation from RaC' extends to a distance of 0·033 mm from the central inclusion.

The exceedingly long interval of time during which small inclusions have existed in certain samples of mica makes it possible in such cases to detect the action of an amount of radium as small as 10^{-17} gm. This amount is one hundred thousand times smaller than the amount determinable by electrical means. In age determinations we must of course also know the amount of radioactive material contained in the inclusion, in addition to the depth of coloration. This cannot be determined directly, but from a knowledge of the mineral of which the inclusion is composed, and by measuring its size with a microscope, an estimate of the quantity of radioactive matter in the inclusion can be formed. In this way the age of mica from Devonian rocks has been calculated to be 400 millions of years. By the uranium-lead method the age of the Devonian has been found to be about 360 millions of years, a value in good agreement with that just mentioned.

All the radioactive methods of age determination postulate the invariability of the rate of decay of uranium, and we have no reason to doubt the justification of this assumption at present. Of the three methods of age determination described, the most reliable one is undoubtedly that based on the evaluation of the content in the mineral of the solid end-product (lead), and particularly when we find the uranium-lead content of uranium minerals free from thorium.

2. The Distribution of Radioactive Substances

It has already been pointed out in the chapter on the extraction of radioactive substances that uranium and thorium minerals serve as sources for all the radio-elements of long life.   At the same time we described in particular the extraction of radium from pitchblende and from carnotite.   It will serve a useful purpose if we now give a summary of the more important uranium and thorium minerals, which may be used for the extraction of radium, mesothorium and their disintegration products.

It is noteworthy that minerals like bröggerite and thorianite, which are both very old and strongly radioactive, have been able to retain their original atomic arrangement completely, or at least for the most part.   Nevertheless, it can be calculated that in bróggerite about every eighth uranium atom has disintegrated since the mineral was formed, and the crystal lattice has been traversed by about as many a-particles as there are uranium atoms contained in the lattice (8).

Small quantities of thorium, uranium and of their disintegration products can be detected in rocks, in fresh and in sea water, in the atmosphere, and in certain of the heavenly bodies.   For establishing the presence of thorium or uranium we generally measure the amount of thorium or radium emanation present in the material, since these can be readily recognised.

The mean uranium content of 1 gm. of rock in the earth's crust amounts to $6 . 10^{-6}$ gm., the radium content being $2 . 10^{-12}$ gm. The former value is calculated from the latter, and both vary with the nature of the rock, the more exact radium values being $0.8 . 10^{-12}$ gm. for an ultra-basic rock, and $3.5 . 10^{-12}$ gm. for an acid rock (9). The thorium content of rocks is somewhat in excess of the uranium content, and amounts to $1.6 . 10^{-5}$ gm. per gm. of rock

The quantity of energy developed annually by radioactive processes in each cc. of the earth material in the outer crust amounts in mean to 1,000 ergs.   It falls off rapidly when we penetrate to the deeper strata, and the average value is estimated to be about 10 ergs (10).

The radium content of sea water is about a thousand times smaller than that of the earth's crust, and varies between $0.25 . 10^{-15}$ and $26 . 10^{-15}$ gm. per cc., whereas the thorium content, so far as it has been measured (Adriatic Sea), has been found to vary between about 10^{-7} and $5 . 10^{-7}$ gm. per cc. (11).

TABLE XXXIII

Summary of the More Important Radioactive Minerals (7)

Name of Mineral	Chemical Constitution	Hardness	Specific Gravity	Cryst. System	Uranium Content (%).
Uraninite (pitch-blende)	$(UPb_2)_3U_2O_{12}$	3—6	5—9	cubic	65-90 uranium oxide, up to ca. 10 % ThO_2, 5-10 % PbO, and frequently small quantities of one third of all the known chemical elements.
Carnotite	$K_2O.2U_2O_3.V_2O_5.3H_2O$	—	—	rhomb	62.7 $(UO_2)O$.
Autunite (calcium-uranium-mica, calcium-uranite)	$CaO.2(UO_2)O.P_2O_5.8H_2O$	1—2	3—3.1	rhomb	
Barium-uranite (urano-circite)	An autunite with barium instead of calcium				
Chalcolite (copper-uranium-mica, copper-uranite)	$CuO.2(UO_2)O.P_2O_5.8H_2O$	2—2.5	3.5—3.6	tetrag.	61 $(UO_2)O$.
	Uranum ochre = sulphur- to lemon-yellow powdery deposit on uranium pitchblende. Much rarer are Broggerite, Cleveite, Nivenite (thorium-uraninite), with 55-66% U, 7.62-13.87 % lead, 3.5-6.5 % thorium, and other elements.				
Monazite	$(Ca.La.Di)PO_4$, with thorium	5—5.5	4.9—5.5	mon.	Up to 18 % ThO_2, and 31.3 % CaO.
Thorite (orangite)	$ThSiO_4(+aqua)$	—	4.4—4.7	tetrag.	Up to 81.5 ThO_2, and varying uranium content.
Thorianite	$(ThU)O_2$	5.5—6.5	8.0—9.7	cubic	The richest thorium mineral, with 46.5 % Th, and up to 48 % U.

Much greater activities are found in a few " radioactive " spas and thermal springs (12). Their greater radioactivity is due to radium emanation, which has been taken up by the water in its passage through rocks of good emanating power, and containing radium. For this reason, the activity is not constant. One of the most active waters is that from the Joachimstal mines ; it contains $7 . 10^{-10}$ Curies or 2050 Mache units per cc. The activities of a number of springs are given in Table XXXII. (p. 179).

Since the soil always contains radium, emanation is constantly diffusing from it into the atmosphere. The higher we rise above the ground, the less is the amount of available emanation and its disintegration products, in consequence of their decay (13). Whereas the emanation content of the air escaping from the soil has a mean value of $3 \cdot 6 . 10^{-14}$ Curies per cc., the highest emanation content that has been found in free air has only one hundredth of this value, the mean value being $8 . 10^{-17}$ Curie/cc., or about $1 \cdot 3$ atoms per cubic centimetre. From this result we can make a rough estimate of the quantity of radium from which the whole of the emanation in the atmosphere has been derived ; the resulting value is 1000 kgm. On the other hand, the mean value of the radium emanation content in the air over the oceans has been found to be only $2 \cdot 6 . 10^{-18}$ Curie/cc. (14). The number of pairs of ions produced per second in each cc. of the atmosphere over land surfaces is about 10, but this number is found to vary somewhat with the material of the measuring apparatus. Over the Pacific and Atlantic Oceans about $3 \cdot 8$ pairs of ions/cc./sec. were found, and with the use of an ionisation vessel of ice $2 \cdot 6$ pairs of ions/cc /sec. were found in the air over Lake Ontario (15). The amount of emanation given up per second by 1 sq. cm. of the surface of the sea is $1 \cdot 04 . 10^{-17}$ Curies, whereas the corresponding value for land is 2 to $3 . 10^{-17}$ Curies.

The connection between the emanation content of the air and meteorological factors (air pressure, temperature, etc.) is not yet known to any degree of finality. Moreover, it has been suggested recently that part of the radioactive material found in the atmosphere may be of cosmic origin (16).

A small activity is also found in atmospheric precipitation. Rain and snow do not carry with them the gaseous emanation, but its solid disintegration products that are in suspension in the atmosphere, and in this way they derive their activity.

The order of magnitude of the radium content of stone meteorites

is a little higher than that of ultrabasic rocks in the earth. This fact indicates that the radioactive elements are also present in the heavenly bodies. The average radium content of stone meteorites amounts to about $\frac{1}{4}$ of the value for granite, and iron meteorites generally contain less than one tenth of the amount found in stone meteorites (*17*). Definite spectroscopic proof of the occurrence of radium in the stars has not yet been obtained.

3. THERMAL CONSEQUENCES OF THE DISTRIBUTION OF RADIOACTIVE SUBSTANCES

We have seen that radioactive substances are distributed throughout the whole of the earth's crust, and since the development of heat accompanying the decay of these substances is quite considerable, it follows that they must make themselves felt in the heat content of the earth.

The earth is losing heat continuously by radiation. Since we know the rate of increase of temperature with depth in the earth's crust, we can calculate the amount of heat radiated, and hence also the quantity of uranium which, by virtue of its heat of disintegration, would suffice to compensate for the total thermal radiation from the earth. The amount is not excessively large ; it has the value $2 \cdot 4 \cdot 10^{20}$ gm. uranium, or $9 \cdot 10^{20}$ gm. thorium. This is about 150 times smaller than the amount of uranium calculated for the whole earth, on the assumption that we may employ in this calculation the average uranium content found in ordinary rocks. From this lack of agreement, and in accord with geological considerations, it follows that the uranium content of the earth's crust must diminish with depth. In any case, the uranium- and hence also the radium-content of the whole earth is not greater than that of a shell of 16 km. thickness, having a radium content equal to that of the surface rocks. If only part of the earth's heat is of radioactive origin, the thickness of this shell works out to be even smaller (*18*).

On the other hand, the heat radiated by the sun cannot be wholly attributed to the development of heat resulting from atomic disintegration, unless we assume the presence of disintegration processes unknown on the earth, or that uranium and thorium disintegrate more rapidly in the sun that in the earth. Even if the sun consisted exclusively of uranium, the amount of heat resulting from its disintegration would only account for half of the amount of heat radiated.

4. ELECTRICAL CONSEQUENCES OF THE DISTRIBUTION OF RADIOACTIVE SUBSTANCES

The *intensity of ionisation, i.e.* the number of pairs of ions formed per unit volume and per unit time, is of importance for the elec-trical state of the atmosphere, and this in turn is closely related to other meteorological conditions. This ionisation number for the atmosphere can be calculated from the conductivity of the air, the mobility of the ions, and their coefficient of recombination. The normal intensity of ionisation of the atmosphere is found to be $1·5$ ions cm.$^{-3}$ sec.$^{-1}$, and to produce this number of ions we should require $6 . 10^{-17}$ Curie cm.$^{-3}$ of emanation, together with its disintegration products (*19*). We have already seen that an amount of emanation of this order is always present in the atmosphere, from which we may conclude that the ionisation of the atmosphere is mainly due to the radiation from the active substances contained in it.* Other factors may be involved in a slight degree, such as the very penetrating nebular γ-radiation (*20*) detected at high levels in the atmosphere, the intensity of which constantly diminishes as we approach the earth's surface. This penetrating radiation has been studied in greater detail during balloon flights, on high mountains, and recently in the laboratory by using electrometers of special construction and high insulation ; its absorption coefficient was found to be ten times smaller than that of the penetrating γ-radiation from RaC (*21*).

It has been pointed out recently that β-particles emitted by the radioactive constituents of the atmosphere will be accelerated in the fields of thunderclouds, even if the original direction be almost at right angles to that of the field. Potential differences of many millions of volts are likely to develop in thunderclouds, and a favourably moving electron may rapidly gain kinetic energy until put out of action by an exceptional encounter. Occasionally, such an electron may acquire sufficient kinetic energy to render its effective mass comparable with that of a hydrogen nucleus. Under such circumstances it may be capable of bringing about atomic disruption or of combining with a nucleus. Moreover, thunderclouds may possibly be the seat of extremely penetrating β- or γ-radiation, and this may be a contributory factor in the penetrating radiation referred to in the previous paragraph (*22*).

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* Less than one α-particle per hour has been registered in an experimental vessel of 40 litres capacity freshly filled with carbon dioxide.

5. Optical Consequences of Atomic Disintegration in the Sun. The Aurora

The aurora is associated with the periodic variations in the activity of sun spots, and encircles the magnetic north and south poles of the earth. These facts suggest that we can interpret it as being due to electrically charged corpuscular rays emitted by the sun, which, when they arrive in the neighbourhood of the earth, are deflected by its magnetic field (23). These corpuscular rays are presumably of radioactive origin. Groups of rays of different velocity have been detected in the aurora, but it is still an open question whether they are high-speed electrons or positive atomic rays of moderate velocity (24).

XXVII

THE HISTORICAL DEVELOPMENT OF THE SCIENCE OF RADIOACTIVITY (1)

On the 24th of February, 1896, Henri Becquerel read a paper before the Academy of Science in Paris, in which he stated that compounds of uranium emits rays that are able to affect a photographic plate through material opaque to light. This casual observation was the starting-point in the development of a new branch of knowledge, viz. radioactivity.* After Becquerel's discovery, numerous substances were tested for similar properties to those shown by uranium, and as a result the radioactivity of thorium was discovered by C. G. Schmidt and Mme. Curie (1898). In the same year, the systematic investigation of different uranium materials led Pierre Curie and his wife to the discovery of two markedly strong active substances in pitchblende, one of which was separated along with bismuth and was called " polonium," whereas the second, radium, was found to give similar reactions to salts of barium. Further investigations revealed the fact that it is very difficult to concentrate polonium (Marckwald), and that radium is a substance that is sufficiently long-lived to permit of its preparation in weighable quantities, and at the same time sufficiently short-lived to show in a high degree the typical properties of a radio-element. In addition to these, radium showed several other favourable properties, such as the production of a succeeding gaseous product of not too short life, etc. From amongst the most important of the remaining radioactive substances, first actinium (1899) was discovered by Debierne and by Giesel, then radiothorium (1905) and mesothorium (1907) by Hahn. In the year 1907 ionium was discovered in uranium minerals by Boltwood

* Becquerel was investigating all kinds of fluorescent substances, because at that time a connection was thought to exist between fluorescence and Rontgen radiation, but the new radiation was first found with fluorescent salts of uranium. He recognised later that all salts of uranium send out rays, so that fluorescence has nothing to do with the new phenomenon. As has often happened in the history of science, this discovery constituted what Lodge (?) has termed " deserved good fortune."

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and almost simultaneously by Hahn and Marckwald, and in the same year N. R. Campbell succeeded in establishing the radioactivity of potassium and rubidium. The discovery of an additional radio-element of long life, viz. protactinium, was not made until the year 1918, by Hahn and Meitner, and by Soddy and Cranston. The production of heat by radium was observed early on, but first measured in the year 1903 by Curie and Laborde ; a particularly accurate determination of this important quantity resulted later from the investigations of Schweidler, St. Meyer and Hess, and Rutherford.

By the discovery of radio-active substances a new and powerful field of natural phenomena was opened up, but at first there was lacking a satisfactory linking together of the numerous and inexplicable individual phenomena with each other, and with the phenomena of other physico-chemical branches of knowledge. Light was first shed on these by the disintegration theory, formulated by Rutherford and Soddy in the year 1903. According to this theory, the emission of radiation by radioactive substances is a phenomenon consequent upon atomic transformation, and the theory made it possible to deduce quantitative information on the process of transformation, from the nature and intensity of the radiation. The idea of a development of inorganic matter had frequently been conjectured in the course of the history of chemistry, and by virtue of the disintegration theory and the unbounded evidence in its favour, it has established itself permanently in the fabric of our knowledge. The disintegration theory of Rutherford and Soddy has thereby achieved the distinction of becoming one of the most important theories in Natural Science.

The investigations that resulted from the formulation of this theory at first proceeded mainly in two directions. First it was necessary to examine the nature of the rays from radioactive substances, and then to reveal the sequence of the transformation processes and the properties of the radio-elements.

In 1899 Giesel, St. Meyer and Schweidler, and H. Becquerel had already established the fact that part of the radioactive rays could be deflected in a magnetic field. A few years later, Rutherford and his co-workers succeeded in identifying the exact nature of the a-, β- and γ-rays. Of particular importance for the recognition of the nature of the a-rays was the work of Ramsay and Soddy, and of Rutherford and Royds, who showed that they were charged atoms

of helium. P. Curie had already observed that they have a definite
range, and the study of the absorption of the rays was mainly the
work of W. H. Bragg, Geiger, Marsden, Kleeman, Mme. Curie and her
collaborators (including Mlle. I. Curie), Rausch von Traubenberg
and others. Elster and Geitel on the one hand, and Crookes on the
other, made the observation that α-rays are able to excite scintilla-
tions in zinc sulphide screens, and this proved to be of great practical
importance. Regener was the first to make quantitative counts of
α-particles, and in a similar way, Rutherford and Geiger succeeded
in determining the number of α-particles emitted by 1 gm. of radium,
and also the charge of an α-particle.

More detailed information on the properties of the β-rays was
obtained primarily in the laboratories * of Lenard (Heidelberg),
J. J. Thomson (Cambridge), Rutherford (Montreal, Manchester and
Cambridge), Crowther (Cambridge and Reading), Hahn, Meitner,
v. Baeyer and Geiger (Berlin), Danysz and de Broglie (Paris), Kovarik
(New Haven), and A H. Compton (Saint Louis), and of the γ-rays by
Rutherford and his co-workers, by W. H Bragg (Adelaide, Leeds and
London), and from investigations in the Vienna Radium Institute
(K. W. F. Kohlrausch, Hess, Lawson and others). The method of
C. T. R. Wilson (Cambridge) for rendering visible the tracks of the
rays has been of great service in the study of all three types of rays.

The phenomenon of recoil, which was discovered by Hahn and by
Russ and Makower, and investigated later particularly by Werten-
stein, made possible the isolation of several elements of short life.
The relation between range and disintegration constant, discovered
by Geiger and Nuttall in 1911, has proved to be very important in
revealing the existence and for determining the period of elements
both of very short and of very long life.

The nuclear theory of the atom, which is of paramount importance
in modern physics, was advanced in the same year by Rutherford.
It was based on observations by Geiger on the scattering of α-rays
in their passage through matter, and furnished a satisfactory explana-
tion of this phenomenon. But on the basis of the classical ideas of
theoretical physics it was not possible to interpret the properties or
the stability of such a structure. Not until two years later was this
achieved by Bohr, who utilised Planck's quantum theory for this
purpose. He postulated the invalidity of classical electrodynamics

* When more than one place is mentioned, the last is the one now
valid.

in the case of atomic processes. According to Bohr, the stability of the atom is due to the existence of certain privileged states of motion of a quantum nature for the electrons revolving round the nucleus, and the processes of the emission and absorption of light are intimately connected with these states. The resulting quantum theory of the atom made it possible for the first time to interpret emission and absorption spectra in a simple and numerical fashion. Moreover, the theory also led to the interpretation of that vast field of knowledge embodying the collisions between electrons and atoms, which was opened up by the work of Franck and Hertz. The formulation of the principle of correspondence by Bohr (1918) marked a further step of the greatest significance. Thus it was now possible to gain insight into the regularities and also the exceptions (rare earths) revealed in the periodic classification of the elements.

The development of the study of Röntgen rays is also closely related to the modern theory of the atom. The notable discovery of v. Laue (1911) was soon followed by the work of W. H. and W. L. Bragg on the reflexion of Röntgen rays in crystals, and by Moseley's investigation on the characteristic Röntgen lines of the elements, by virtue of which the fundamental importance of the atomic number was established (1913). But radioactivity itself also owes a debt to the development of Röntgen spectroscopy. Thus the measurement of the wavelength of γ-rays, carried out by Ellis, Meitner, and others, first became a practical proposition when the spectroscopy of Röntgen rays had made it possible to localise the individual groups of electrons in the extra-nuclear structure of the atom, and to calculate the work necessary to separate an electron from the atom. Only in the case of soft γ-rays had Rutherford and Andrade succeeded previously in carrying out a determination of the frequency by the crystal method.

Meanwhile the science of radio-chemistry had also made important advances, investigations by Marckwald, Keetmann, Boltwood, Auer v. Welsbach, McCoy, Strömholm and Svedberg, Fleck and others led to a conception held notably by Soddy even in the year 1910, namely, the existence of radioactive elements, later called "isotopes," which, in spite of differences in their atomic weights and radioactive properties, at the same time show the same chemical, electro-chemical and spectroscopic properties. On the basis of this view, and with the aid of more complete knowledge of the sequence

of disintegration in the transformation series of the radio-elements, the radioactive displacement laws were first formulated by A. S. Russell, and almost simultaneously by Fajans and by Soddy (1913), the results of the last two authors being satisfactory in every detail. Amongst other things, these laws made it possible to settle the question as to the end-products of the disintegration series, and the conclusions formed in the course of this work were completely confirmed by atomic weight determinations carried out by Richards, Hönigschmid and others. It became more and more clear that these results are of the greatest importance not only in radio-chemistry, but also in general chemistry. It became necessary to limit the idea of a chemical element to its chemical inseparability, and even in the case of the ordinary elements it became imperative to reckon with the possibility that they might consist of more than one type of atom.

A few years later, Aston proved by means of his mass spectrograph that the phenomenon of isotopy is actually a general property of the elements   This apparatus was constructed by Aston as a further development of the pioneer work of J. J. Thomson on positive ray analysis.   At the same time, Aston's investigations (1919) revealed the integral nature of atomic weights, and thus eliminated the argument against Prout's hypothesis.   This work constituted a magnificent advance in our knowledge of the structure of matter. Science was confronted by a new problem, namely, to separate the elements occurring in nature into their constituent isotopes.   Only in a few cases has it been possible to solve this problem, and then only to a certain degree.   Furthermore, recent years have seen the initiation of the artificial disintegration of the elements, an achievement first successful in the case of nitrogen, and carried out by Rutherford in 1919.   The investigations of Rutherford and Chadwick, and of other workers, have yielded important information on the structure of atomic nuclei.   This work was carried out partly at the Cavendish Laboratory, and partly at the Vienna Radium Institute (Kirsch and Pettersson).

Success has also been attained in various branches of applied radioactivity.   The chemical effects produced by the rays were investigated by Lind, Duane and Wendt, Kailan, Przibram and others.   Radioactive indicators have frequently been resorted to as an expedient in chemical and physical investigations.   The applications of radioactivity to geological problems have been primarily

the work of Boltwood, Strutt, Joly, Mügge, Holmes and Ellen Gleditsch. In the domain of atmospheric electricity, mention should be made of the work of Elster and Geitel, v. Schweidler, Mache, Eve, McLennan, C. T. R. Wilson, Hess, Kohlhörster, and Gockel.

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